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RECONNAISSANCE STUDY OF RADIOCHEMICAL POLLUTION FROM PHOSPHATE ROCK MINING AND MILLING

National Field Investigations Center
Denver, Colorado

December 1973

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A reconnaissance stydy of the phosphate mining and milling industry was necessary to investigate the magnitude of radiochemical pollution to receiving waters. This report describes the findings of the study and other related problems associated with processing of phosphate fertilizers, such as air pollution, ground-water contamination, possible deleterious consequences of fertilizer use, effects on other receiving water uses, including shellfish and drinking water supplies, and the use of by-product material in the construction industry. Throughout the report a comparison has been made of reconnaissance sampling results with promulgated radiochemical standards and guidelines.

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GLOSSARY OF TERMS

SYMBOLS

Ci - Curie, the basic unit intensity of radioactivity in a sample of material. One Curie equals 37 billion disintegrations per second, or approximately the radioactivity of one gram of radium.

g - weight in grams = 0.002205 pounds

k - kilo, used in conjunction with other symbols as a prefix for thousand = 10^3

km^2 - area in square kilometers = 100 hectares or 0.3861 square miles

l - volume in liters = 0.2642 gallons

m - milli, used in conjuntion with other symbols as a prefix for one thousandth = 10^{-3}

m - length in meters = 3.281 feet or 1.094 yards

man-rem - a unit of exposure dose of gamma radiation

MPC - maximum permissible concentration used in limiting radiochemical materials in air or water

metric ton - equals 1000 kilograms = 2205 pounds

p - pico, used in conjunction with other symbols as a prefix for one millionth of one millionth = 10^{-12}

μ - micro, used in conjunction with other symbols as a prefix for one millionth = 10^{-6}

DEFINITIONS

beneficiation	-	combination of chemical and physical processes applied to an ore to increase the concentration of desired minerals
contaminated water	-	recycled process water used in wet-process phosphoric acid plants for gypsum slurry transport, barometric condenser feed, and flume scrubbers
continuous exposure	-	exposure to radiation for 168 hours per week
half-life	-	the time required for a given amount of a radioisotope to decay to one-half that amount
occupational exposure	-	exposure to radiation during the normal working period, considered to be 40 hours per week
piezometric map	-	a contour map of an imaginary surface to which the water in an artesian aquifer would rise
slurry	-	a mixture of water and solids that can be pumped and that will flow
unrestricted area	-	areas, including residential quarters, for which control is not maintained for the purpose of protecting individuals from exposure to radiation

I. INTRODUCTION

The mining, beneficiation, and milling of phosphate rock is a major segment of the U. S. mining industry, in terms of both tonnage and sales. During 1972, approximately 38.5 million metric tons (42.4 million tons) of phosphate rock were mined in the U.S., an increase of 40 percent from the 27.2 million metric tons (30 million tons) mined during 1968. The U. S. produces approximately 45 percent of the world output of phosphate fertilizers. This production contains over 4.5 million metric tons (5 million tons) of phosphorous. Phosphate rock and phosphate fertilizers are major export items of this country. Much of this export is to Western Europe, Japan, and Israel and has a value of approximately $100 million per year. A large portion is exported in the form of phosphate rock which is subsequently milled to produce phosphate fertilizers at the point of use.

The United States is one of the world's major consumers of phosphate fertilizers, followed by Western Europe and the Communist nations in terms of total phosphate usage.

"Phosphate rock" is a commercial term for a rock containing phosphate minerals, usually calcium fluorophosphate, in sufficient concentration to permit its use in commercial products (Lewis, 1970). It may be of either the sedimentary or igneous form, although the sedimentary form is the more common.

Phosphate rock does not have a definite chemical composition. The major phosphorous minerals of most phosphate rock are in the apatite group and can be represented by the formula $Ca_5(PO_4)_3(F,Cl,OH)$. The

(F,Cl,OH) radical may be any combination of the fluoride, chloride, or hydroxyl ions, while the (PO_4) radical can be partly replaced by the vanadate, silicate, sulfate, or carbonate ions. Rare earths, chromium, and uranium are other common impurities. Uranium concentrations vary directly with the phosphate concentration of phosphate rock and usually are in the range of 40 to 165 grams of uranium per metric ton (0.1 to 0.4 pounds/ton) of rock (Bates, 1969). This uranium was deposited contemporaneously with the phosphate rock and is incorporated in the grain structure. Uranium was recovered from phosphoric acid produced from phosphate rock on a commercial basis at three plants during the 1950's (Kennedy, 1967). Two plants are currently in the construction or planning stage for the recovery of uranium from phosphoric acid. The presence of uranium in phosphate ore is used to advantage in gamma-ray prospecting for new phosphate rock deposits.

Since natural uranium contains approximately 99.28 percent uranium-238 and 0.71 percent uranium-235, the decay chain of uranium-238, known as the uranium-radium family, is of primary importance. The isotopes formed from uranium-238 are shown in Figure 1 along with their mode of decay and half-life and present varying degrees of hazard. From the standpoint of water pollution, the radioisotope radium-226 is the most hazardous. It has a maximum permissable concen-tration (MPC) an order of magnitude less than any of the other decay isotopes. Phosphate rock contains approximately 50 microcuries of radium per metric ton (45 microcuries per ton).

Radium tends to replace calcium in bone. It was shown to be of

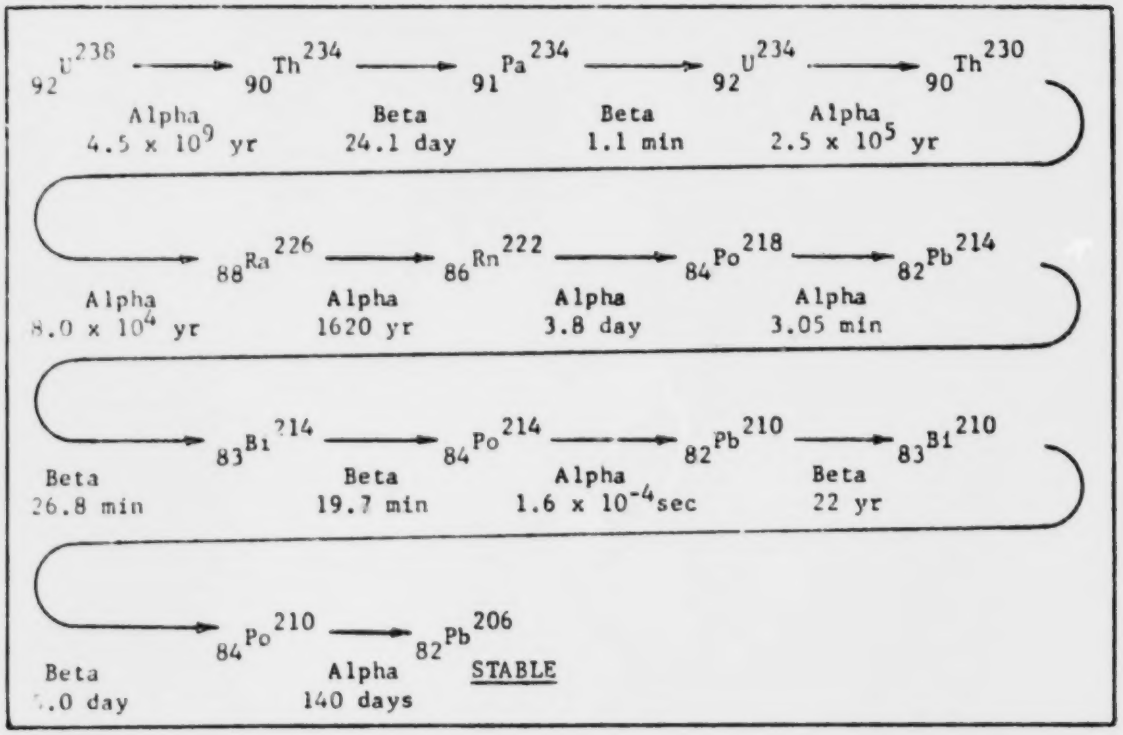
$_{92}U^{238}$ → $_{90}Th^{234}$ → $_{91}Pa^{234}$ → $_{92}U^{234}$ → $_{90}Th^{230}$
Alpha 4.5 x 10^9 yr
Beta 24.1 day
Beta 1.1 min
Alpha 2.5 x 10^5 yr
$_{88}Ra^{226}$ → $_{86}Rn^{222}$ → $_{84}Po^{218}$ → $_{82}Pb^{214}$
Alpha 8.0 x 10^4 yr
Alpha 1620 yr
Alpha 3.8 day
Alpha 3.05 min
$_{83}Bi^{214}$ → $_{84}Po^{214}$ → $_{82}Pb^{210}$ → $_{83}Bi^{210}$
Beta 26.8 min
Beta 19.7 min
Alpha 1.6 x 10^{-4} sec
Beta 22 yr
$_{84}Po^{210}$ → $_{82}Pb^{206}$
Beta .0 day
Alpha 140 days
STABLE

Figure 1. Uranium-Radium Family (FWPCA, 1966)

prime importance in the control of radiochemical pollution from uranium mills throughout the Southwest (FWPCA, 1966). As a result, a great amount of effort was expended in stabilization of tailings piles from the various uranium mills in the Colorado River Basin. Measures such as chemical coatings, soil cover, and vegetative stabilization were employed.

Radium-226 decays by alpha emission into radon-222, a radioactive gas with a half life of 3.8 days. The decay products of radon-222, in turn, are particulates which can be adsorbed onto respirable particles of dust. Radon and its decay products has been implicated in an increased incidence of lung cancer in those workers exposed to high levels (Bureau of Mines, 1971). Heating or grinding of phosphate rock would liberate radon and its decay products to the surrounding atmosphere.

It is generally agreed that unlike other materials, there is no threshold value for radiation exposure. Accordingly, the Federal Radiation Council has repeatedly stated that all radiochemical material releases are to be kept to the minimum practicably obtainable. The Council states "It should be general practice to reduce exposure to radiation, and positive efforts should be carried out to fulfil the sense of these recommendations. It is basic that exposure to radiation should result from a real determination of its necessity (Federal Radiation Council, 1960)."

From the information available it was determined that a reconnaissance study of the phosphate mining and milling industry was necessary to investigate the magnitude of radiochemical pollution to

receiving waters. This report describes the findings of the study and other related problems associated with processing of phosphate fertilizers, such as air pollution, ground-water contamination, possible deleterious consequences of fertilizer use, effects on other receiving water uses, including shellfish and drinking water supplies, and the use of by-product material in the construction industry. Throughout the report a comparison has been made of reconnaissance sampling results with promulgated radiochemical standards and guidelines.

II. PHOSPHATE ROCK MINING AND MILLING AND WASTE SOURCE DESCRIPTION

The comprehensive work on the occurrence and milling of phosphate rock into phosphoric acid and phosphatic fertlizers is the book by W. H. Waggaman (1952), titled "Phosphoric Acid, Phosphates and Phosphatic Fertilizers". Additional information is contained in U. S. Bureau of Mines Information Circulars 7814 (Ruhlman, 1958) and 7951, (Waggman and Ruhlman, 1960). All of these reports, and others (McKelvey, 1967, and Menzel, 1968) contain mention of the widespread occurrence of uranium in phosphate rock.

The U. S. Environmental Protection Agency (EPA) and the U. S. Public Health Service (PHS) have commissioned a number of studies of the pollutional aspects of phosphoric-acid manufacture. Two of these (Manufacturing Chemists Association and Public Health Service, 1968 and 1970) deal with the air pollution problems associated with the industry. Two EPA grants (Battelle Memorial Institute, 1971 and Datagraphics, Inc., 1971) deal with the liquid waste components of the phosphate industry. The radiation problem is not addressed in these documents.

Phosphate rock deposits are well distributed throughout the world but those satisfying current world requirements, for the most part, are located in the United States, North Africa, and Russia. Large, undeveloped deposits in Peru, Spanish Sahara, and Australia are expected to be exploited in the future.

In the United States, 83 percent of the phosphate mining in 1968 was done in Florida and North Carolina, with the bulk of this done in

Florida (Bates, 1969). Tennessee supplied 6 percent of the 1968 national production, and deposits in the inter-mountain West supplied 11 percent. The Tennessee deposits are near depletion and are expected to become less important in future years while the North Carolina deposit will assume greater importance. The locations of phosphate mining and milling areas throughout the nation are shown in Figure 2. Much of the phosphate mined in the Tennessee, North Carolina, and Western mining areas is converted to fertilizer near the site of the mining. A major portion of the Florida rock is transported by barge throughout the U. S. and milled at areas near the site of use. Barge transportation is required for economical movement of the raw rock.

MINING

The mining techniques [Figure 3] employed in the various mining areas are different, and are dependent upon geologic and hydrologic conditions which exist at the mine site. The impurities which are present in the phosphate rock vary from place to place.

In the Florida land-pebble deposits, the overburden is removed and the ore mined by large electric draglines. The ore is slurried and pumped to the washing plants which are often located several kilometers from the mines. Those particles less than the 200-mesh size, called slimes, are discharged from the washing plant. In the Florida field located south of Lakeland, the slime slurry frequently comprises up to 1/3 of the total mined tonnage (Lewis, 1970). The slimes are similar in chemical composition to the original ore matrix, but are

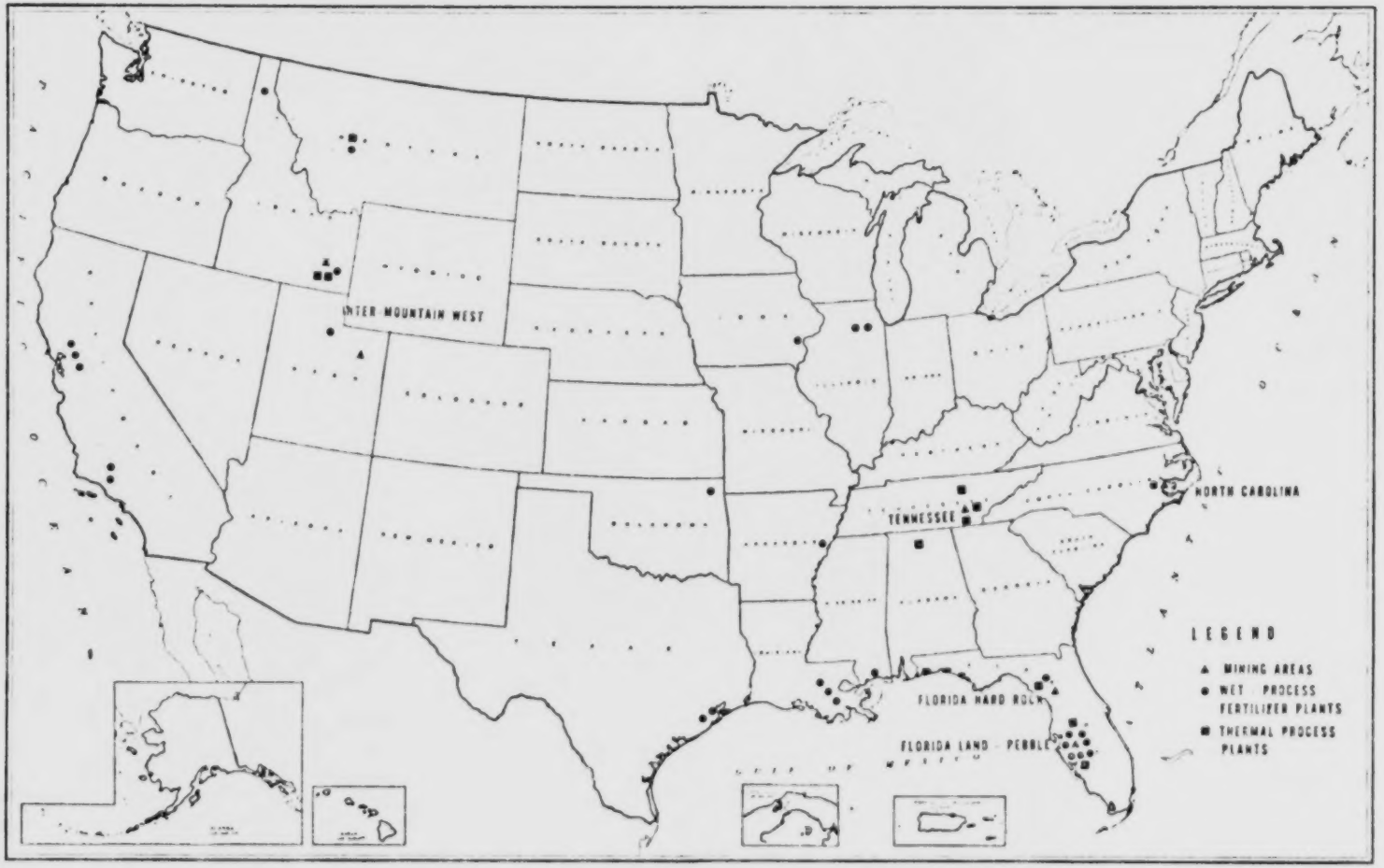

Figure 2. Major Phosphate Rock Mining and Milling Sites

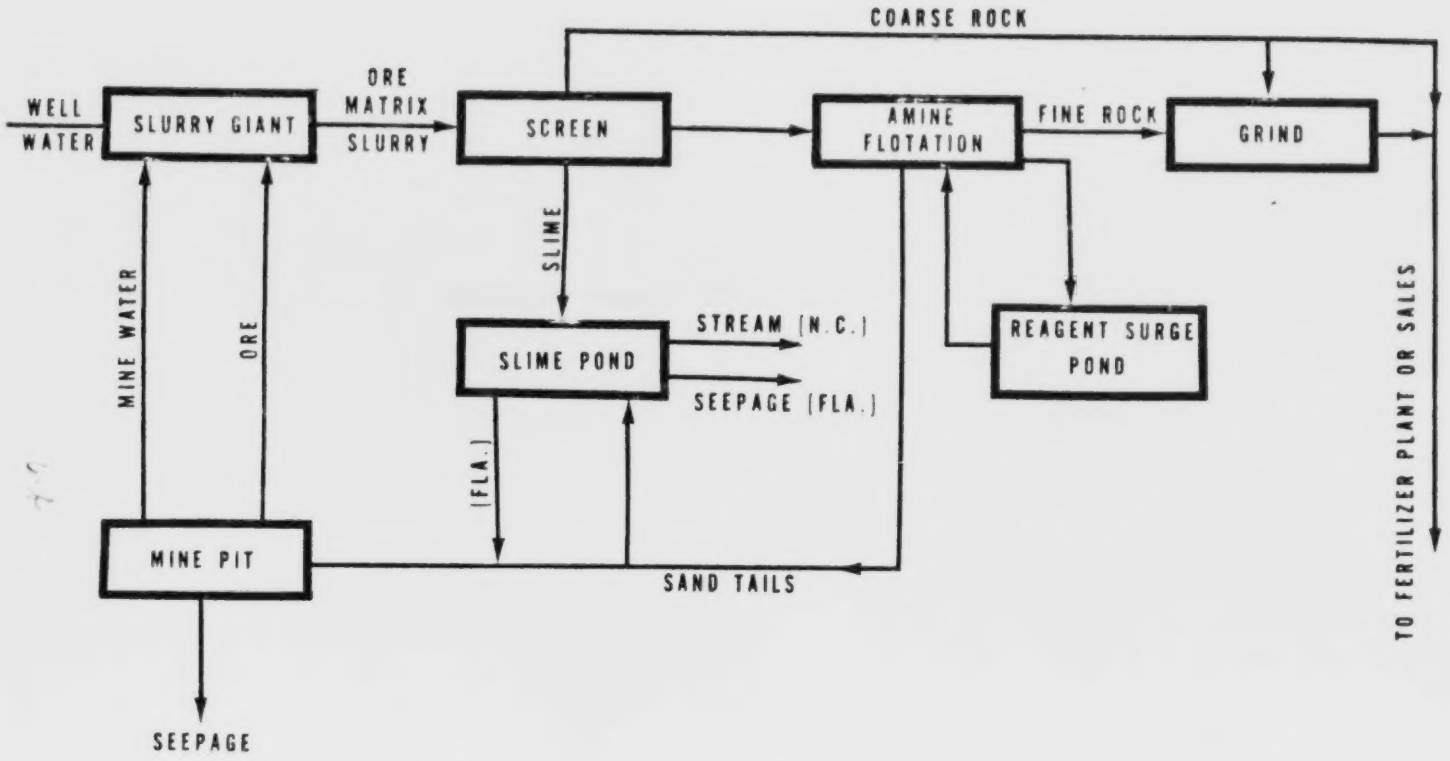

Figure 3. Flowsheet, Florida and North Carolina Phosphate Rock Mining and Beneficiation

extremely difficult to treat or dewater. The resultant slurry of clay-size slime particles and water occupies a volume much larger than the original volume of the ore. Mined-out pits are frequently used for storage of a portion of the slime slurry, however additional storage volume, in the form of surface ponds is usually required. Frequent breaks of the slime pond dikes have plagued the Florida mining industry.

The material larger than 200-mesh is treated in an amine flotation circuit. In this procedure, the silica sand in the ore is separated and either slurried to sand piles, used in construction of the perimeter of the slime ponds, or placed in mined-out areas. The spent amine flotation water is discharged to mined-out areas and recycled. The separated phosphate rock is then either sold for export or sent to a phosphate mill for further processing.

In North Carolina the mine located near Aurora has a number of high-capacity wells that are continuously pumped. This pumpage permits dry mining by lowering the water table almost 60 meters (200 feet), to below the ore level. A 55 cubic meter (72 cubic yard) dragline is used for stripping overburden and piling the ore on the mine surface. A smaller dragline then moves the ore to the site of a hydraulic ore washer. Water from the dewatering wells is used for ore slurry and slime transport, and then discharged into the Pamlico River. Any seepage from the ponds moves toward the mine when it is pumped from the dewatering wells. The amine flotation circuit is a closed system, with no surface discharge.

The North Carolina operation involves movement of a greater amount

of overburden than at the Florida mines. North Carolina ore is similarly screened and floated in an amine flotation circuit. The North Carolina slimes dewater much more easily than do Florida slimes which eliminates the need for extensive slime storage. The solids are retained on a single slime storage pile.

The Tennessee and intermountain mining districts both generally involve dry mining techniques, utilizing shovels for ore removal and trucks for ore transport. Much of the western ore is of sufficient grade to permit direct use without beneficiation (Bates, 1969). Mining in these districts does not have a great potential for water pollution.

MILLING

Following mining and amine flotation, the phosphate rock must be converted into a relatively soluble product by use of either of two methods. The first is acid treatment which consists of reacting the phosphate rock with various acids. The second consists of either thermal reduction of the phosphate rock or other thermal treatment. The major phosphate mills in the U. S. are given in Table 1.

Wet Process Acid and Fertilizer Manufacture - In wet process plants [Figure 4], phosphate rock is reacted with acid, generally sulfuric, to produce phosphoric acid and a waste product hydrated calcium sulfate (gypsum) (Lewis, 1970). The acidulation reaction is given by Equation (1).

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 2HF + 6H_3PO_4 \quad (1)$$

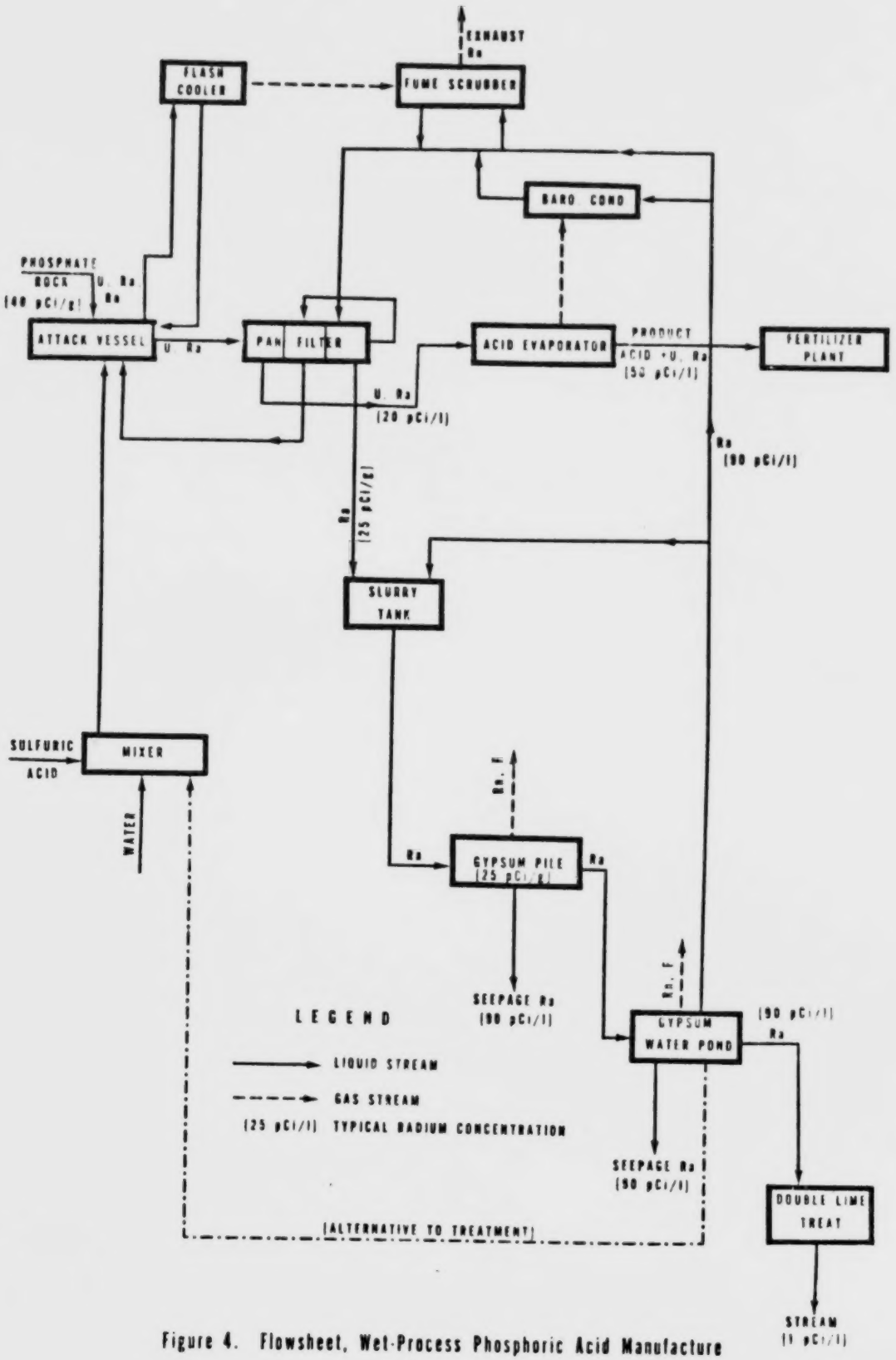

Figure 4. Flowsheet, Wet-Process Phosphoric Acid Manufacture

TABLE 1

MAJOR PHOSPHATE ROCK MILLS
IN THE UNITED STATES

Company	Location
WET PROCESS PHOSPHORIC ACID PLANTS	
W. R. Grace	Bartow, Fla.
Allied Chemical Corp.	Geismar, La.
ARKLA	Helena, Ark.
Borden, Inc.	Piney Point, Fla.
C. F. Industries, Inc.	Bartow, Fla.
Mobil Oil Corp.	Depre, Ill.
Olin Corp.	Pasadena, Tex.
Royster Co.	Mulberry, Fla.
Stauffer Chemical Co.	Pasadena, Tex.
Texasgulf	Aurora, N.C.
Gardinier, Inc.	East Tampa, Fla.
Freeport Chemical Co.	Uncle Sam, La.
Atlantic Richfield Co.	Ft. Madison, Iowa
Becker Industries Corp.	Marseilles, Ill.
National Phosphates (Hooker Chemical, Becker)	Taft, La.
Agricultural Products Corp. (El Paso Products Co.)	Conda, Idaho
Borden, Inc.	Streator, Ill.
Farmland Industries, Inc.	Green Bay, Fla.
Mississippi Chemicals Corp.	Pascagoula, Miss.
N. Idaho Phosphate Co. (Bunker Hill Co.)	Kellogg, Idaho
Occidental Chemical Co.	Lathrop, Calif.
Occidental Chemical Co.	White Springs, Fla.
Olin Corp.	Joliet, Ill.
Penzoil United, Inc.	Hunford, Calif.
J. R. Simplot	Pocatello, Idaho
Union Oil of California	Nichols, Calif.
U. S. Steel Corp.	Ft. Meade, Fla.
Valley Nitrogen Producers	Helm, Calif.
Agrico Chemical Co.	So. Pierce, Fla.
U. S. Steel Corp.	Wilmington, N.C.
Central Phosphates, Inc.	Plant City, Fla.
THERMAL PROCESS PHOSPHORUS PLANTS	
Holmes Co.	Pierce, Fla.
FMC	Pocatello, Idaho
Mobil Chemical	Nichols, Fla.
Monsanto Co.	Soda Springs, Idaho
Monsanto Co.	Columbia, Tenn.
Hooker Chemical	Columbia, Tenn.
Stauffer Chemical	Silver Bow, Mont.
Stauffer Chemical	Tarpon Springs, Fla.
Stauffer Chemical	Mt. Pleasant, Tenn.
TVA	Muscle Shoals, Ala.

During the initial acidulation step, ground phosphate rock is mixed with acid in a reactor attack vessel to form phosphoric acid or superphosphate and calcium sulfate. When ordinary superphosphate is the desired product, enough sulfuric acid is used to convert the phosphate into water soluble superphosphate [$Ca(H_2PO_4)\cdot H_2O$]. Calcium sulfate is not separated from the product. To produce phosphoric acid, additional sulfuric acid is added, and the resultant phosphoric acid is separated from the gypsum in a pan filter. Fumes from the exothermic reaction are collected and treated with water scrubbers, with the scrubbers generally fed by contaminated (recycled) gypsum-pond water. A portion of the phosphoric acid can be reacted with additional phosphate rock to produce triple superphosphate or combined with potash or ammonia to produce complex fertilizers.

Available data (Habashi, 1970; Kennedy, 1967; Spalding, 1972) indicates that there is a partitioning of uranium and its decay products during the acidulation step. Virtually all the uranium remains with the fertilizer, while a major portion of the radium and subsequent decay products are removed in the liquid and solids wastes. Technology exists and has been utilized to recover uranium from the raw acid through solvent extraction. This would not, however, have any effect on the radium or radon decay products.

Calcium sulfate in the pan filters is rinsed with weak acid and contaminated water, discharged to a slurry tank, and slurried for transport from the plant. General industry practice consists of discharging the slurry that contains the radium waste to a gypsum pile, decanting the

clarified water from the pile, and recirculating it to the slurry tank. However, three plants (National Phosphate, Freeport Chemical, and Allied Chemical) located on the Mississippi River in Louisiana upstream of New Orleans, are reported to discharge the gypsum slurry directly to the Mississippi River, with no removal of the solids. Because of the soluble nature of gypsum, the calcium sulfate and any radium will subsequently be dissolved into the Mississippi River waters. No direct discharges of gypsum are know to exist at other plant locations in the country. Two other plants (ARKLA at Helena, Ark. and Becker Industries at Marseilles, Ill.) are reported, however, to discharge a slurry decant.

Thermal processes - Thermal processes for producing phosphate consist of both thermal reduction, in which phosphate rock is smelted with a mixture of carbon and siliceous flux in electric furnaces, and processes without reduction that heat phosphate rock with an alkali salt or silica to produce useable products. For the most part, thermal processes for phosphate production do not involve liquid effluents, other than liquid used in scrubbing gaseous streams.

Radon and its decay products are liberated during the thermal processing of phosphate rock. This radon gas may pose occupational hazards in the immediate processing area. In addition, it is estimated that up to 10 percent of the incoming radon and decay products are discharged in the stack effluent to the ambient atmosphere (Atomic Energy Commission, 1970 and Lammering, 1972).

Other Uses - There are many other uses for phosphate rock which do not use either the wet-process or thermal process. The largest of these

is the production of defluorinated phosphate rock (DPR) for animal feed supplements. In this procedure, phosphate rock is calcined to liberate fluorine which is present in all phosphate rock. A study by Wabashi (1967) indicates that a beef animal fed a daily ration of one half kilogram DPR would receive approximately 20 times the permissible intake of uranium. No data were given on the radium burden, but it would be relatively higher than the uranium burden.

By-product gypsum that contains radium is presently being used as an inferior grade of wallboard in parts of Europe and Japan. This represents a potential environmental hazard which will be discussed later.

III. RADIATION GUIDELINES AND STANDARDS

Numerous guidelines, recommendations and standards for protection against radiation have been published by the Atomic Energy Commission (AEC) and various committees such as the National Committee on Radiation Protection (NCRP), International Commission on Radiological Protection (ICRP), and Federal Radiation Council (FRC). The following summary provides an indication of the quantities of Ra-226 allowable in the water environment as established by a variety of sources:

(1) The PHS Drinking Water Standards (1962) provide standards applicable to potable water used by carriers subject to the Federal Quarantine Regulations. However, these have frequently been used as a ready reference for guidance on water quality limits where other standards do not exist. The limit for Ra-226 in drinking water is 3 picocuries per liter (pCi/l). However, at or about this level, a water supply may still be approved if surveillance of total intakes of radioactivity from all sources are within limits recommended by the FRC for control action. At this concentration a daily water intake of 2 liters per day would result in an intake of 6 pCi/day in the absence of other sources. The FRC control action includes quantitative surveillance and routine control within the range of 3-30 pCi/day for Ra-226 (Public Health Service, 1962).

(2) The National Bureau of Standards (1959) Handbook 69 provides a series of recommended levels of about 200 radioisotopes for occupation exposure. The handbook indicates a maximum permissible

concentration (MPC) of Ra-226 in water of 10^{-7} uc/cc (100 pCi/l) for continuous exposure to the critical organ, in this case bone. For persons outside the controlled area, this is reduced, to levels not exceeding one-tenth the MPC's for continuous occupational exposure, or 10 pCi/l. This level may be an average of a period of up to one year.

(3) The International Commission of Radiological Protection (ICRP) (1959) recommends the same MPC values as given above in Handbook 69. However, the ICRP recognizes three population groups whereas NCRP recognizes only two. The additional group is the "population at large." The report specifies that concentrations "in air or water, applicable to the population at large, should not exceed one-thirtieth of the MPC values for continuous occupational exposure . . ." Thus, the recommended MPC value for Ra-226 in water for the general population is 3.3 pCi/l.

(4) In 10 CFR 20 (1960) radioisotope levels are presented which apply to AEC licensees. Table II in Appendix "B" of these standards list effluent limits to an unrestricted area for soluble Ra-226 in water of 3×10^{-8} uCi/ml (30 pCi/l), above natural background. This level may be averaged over a period not greater than one year. The level may be reduced by the AEC for specific periods of time if the average daily intake from all sources would exceed the daily intake from air and water at one-third the concentrations in Table II of Appendix "B". Under these circumstances, effluent concentrations could be

reduced to an unspecified level. This in effect would allow the AEC to average concentrations so as not to exceed their specified levels. Other portions of 10 CFR 20 provide that not over 0.1 μCi/day of radium may be discharged into a sanitary sewer system and that not over 0.01 mCi/day of radium may be buried in any one location.

(5) Under Section 304(a)(1) of the Federal Water Pollution Control Act of 1972, EPA is required to publish water quality criteria. In October of 1973, EPA proposed "Criteria for Water Quality" which stated inpart that "When raw water is consumed directly, the maximum acceptable concentration of naturally occurring radionuclides having alpha ray emitting daughters, e.g., radium-226, -228, etc. is 5 pCi/l; and the maximum acceptable aggregate dose to the population served by the water supply is 3,000 man-rem/year, unless the radium-226 activity is less than 0.5 pCi/l" (EPA, 1973).

AEC promulgated regulations (10 CFR 20, 1960) differ from ICRP, NCRP, and FRC recommendations by being regulatory statutes set forth as federal law rather than just recommended guidelines for radiation exposure protection. The regulations establish standards for protection against radiation hazards arising out of activities under licenses issued by the AEC pursuant to the Atomic Energy Act of 1954 and apply to "all persons who receive, possess, use or transfer by-product material, source material, or special nuclear material under general or specific licenses issued by the AEC". A general license is effective without

the filing of applications with the Commission or the issuance of licensing documents to particular persons. Specific licenses are issued to named persons upon applications filed pursuant to the regulations. The use of radioactive material or other sources of radiation not licensed by the Commission is not subject to the regulations. As far as is known, none of the phosphate fertilizer plants are holders of specific AEC licenses although they may be covered by the general license criteria because of presence of "source material." The AEC regulation 10 CFR 40 (1961) defines "source material" as (1) uranium or thorium, or any combination thereof, in any physical or chemical form, or (2) ores that contain by weight one-twentieth of one percent (0.05 percent) or more of (i) uranium, (ii) thorium, or (iii) any combination thereof.

The regulations (10 CFR 20, 1960) further state that in addition to complying with the requirements set forth, licensees should "make every reasonable effort to maintain radiation exposures, and the release of radioactive materials and effluents to unrestricted areas, as far below the limit specified as is practicable." The "limits" are not maximum doses or exposures that can be applied safely with no hazard but are guides for "maximum" exposure. The underlying philosophy of radiation protection is that exposures should be maintained at the lowest practicable limit.

In the case of air quality, both the Bureau of Mines and the Occupational Safety and Health Administration have standards relative to radiation. Both arise, however, in recognition of the occupational

hazard resulting from radon in uranium mining operations. The Bureau of Mines regulations (30 CFR 57) prohibit exposure to airborne contaminants exceeding the threshold limit values in the publication "Threshold Limit Values of Airborne Contaminants". This document, however, incorporates NBS Handbook 69 for permissible concentrations of radioisotopes in air. Exposure to radon daughters is further limited in terms of "working level months" (WLM). A "working level" (WL) is any combination of the short-lived radon daughters which will result in the ultimate emission of 1.3×10^5 million electron volts of potential alpha energy in one liter of air. One WLM results from exposure to one WL for 170 hours. The regulations prohibit an exposure of 6 WLM in any consecutive 3-month period and 12 WLM in any consecutive 12-month period. In addition, with atmospheric concentrations between 1.1 and 2.0 WL, immediate corrective action must be taken, and when above 2.0 workers must be withdrawn until such action is taken.

The Occupational Safety and Health Administration limit occupational exposure in mines to no more than 2 WLM in any calendar quarter and no more than 4 WLM in any calendar year. Applicability of either set of standards to other than mining operations would be questionable.

IV. STUDY RESULTS

BACKGROUND

It is widely known that most phosphate ores contain uranium as an impurity. Uranium and its decay products are likely to be present in the products, or in wastes from the processing of such ores.

A report (Spalding, 1972) obtained from Texas A & M University indicates that significant increases in the uranium concentration of cropland runoff has resulted from fertilizer application. The report concluded that the uranium concentration in the Gulf of Mexico has increased as a result of fertilizer manufacture and application.

During the course of preparation for an industrial waste survey of the Olin Corp. phosphate fertilizer plant at Pasadena, Texas, personnel from National Field Investigations Center-Denver (NFIC-D) noted that the Olin permit application reported alpha activities of up to 600 pCi/l in the Olin effluents. During the survey (August, 1972) radium-226 concentrations up to 12 pCi/l were measured in the effluents, with up to 56 pCi/l in the recirculated gypsum pond water. Olin personnel indicated the pond water was only discharged during the onset of a heavy rain.

Copies of the NPDES permit applications for virtually all phosphoric acid plants were obtained and studied by NFIC-D personnel. Most plants, including those which formerly recovered uranium, indicated in the NPDES application that radioactivity was not present in the plant effluent. However, one plant (Allied Chemical) in Louisiana

indicated a gross alpha concentration of over 6,000 pCi/l, while another of the Mississippi River plants (Freeport Chemical) reported almost 700 pCi/l gross alpha. Both these plants also reported extremely high suspended solids concentrations in the effluent, indicative of the absence of gypsum ponds. It is calculated that each of these plants discharge more radium than did any uranium mill in the Southwest prior to initiation of control measures.

In the fall of 1973, NFIC-D conducted reconnaissance level sampling of solids and liquids in the vicinity of phosphoric acid plants in Idaho, Florida, and North Carolina. The NFIC-D effort was a screening study to assess the relative magnitude of radiochemical problems from the different components of the phosphate industry, in various geographic areas. Undoubtably, further evaluation will be required to define the total radiochemical pollution problem from each phosphate plant. Water sampling was conducted around two mines thought to be representative of mining activity in Florida and one in North Carolina that is the largest phosphate mining operation in the world. Phosphoric acid plants sampled include one in North Carolina, four in Florida, one in Texas, and two in Idaho. These plants have a combined total of over 25 percent of the U. S. production of phosphoric acid, and include virtually all variations in wet-processes, with the exception of direct discharge of untreated gypsum slurry to receiving waters.

Region VI personnel conducted sampling in phosphoric acid plants on the Mississippi River which discharge gypsum slurries to the river. These data are not yet available to NFIC-D.

Limited air sampling was conducted by NEIC-Denver at two Florida wet process plants. Other air sampling data have been collected by AEC and EPA in the vicinity of thermal processing plants. EPA presently has underway a comprehensive sampling effort at Idaho mills.

No sampling was conducted by NEIC-D within thermal processing plants. The proposed effluent guidelines now under consideration by EPA for these plants calls for zero discharge of process water.

FINDINGS

Results of radium analyses of samples collected during the NEIC-D reconnaissance investigation are given in Table 2. Except where noted these analyses were performed at the NEIC-D laboratory. Quality control (Appendix A) was accomplished through the cooperation of NERC-Las Vegas and EPA's Eastern Environmental Radiation Laboratory.

Mining

As previously stated, during 1972 approximately 38.5 million metric tons of phosphate rock were mined in the United States. Based upon observed levels of radium in the ore, this would result in almost 2,000 curies of radium being exposed to the environment.

The mining areas in both Florida and North Carolina practice extensive reuse of water for transport and screening. Results of radium-226 analysis of samples of these waters are given in Table 2. It is emphasized that there are few planned releases of Florida mine waters to surface streams. However, the water does seep into underlying ground water. In general, the mine water was found to be rather

TABLE 2

RESULTS OF RADIUM ANALYSIS
PHOSPHATE MINING AND MILLING AREA SAMPLES

Date	Location	Radium Concentration
	Liquid Samples, Mining Areas	pCi/l
8/13/73	Agrico Payne Creek Mine recirculated water, Fla.	1.5
8/13/73	Agrico Palmetto Mine recirculated water, Fla.	1.1
8/13/73	Agrico Payne Creek Mine pit seepage, Fla.	0.61
8/13/73	Agrico Palmetto Mine pit seepage, Fla.	0.28
8/14/73	Unnamed mined-out pit near Bartow, Fla.	0.4
10/16/73	Texasgulf slime pond decant, N.C.	34
10/17/73	Texasgulf Lee Creek Mine dewatering wells, N.C.	0.09
	Solids Samples, Phosphate Ore	pCi/g
8/13/73	Agrico Payne Creek Mine slimes, Fla.	44
8/13/73	Agrico Palmetto Mine concentration, Fla.	38
8/14/73	Royster ore, Mulberry, Fla.	48
8/14/73	C F Industries ore, Mulberry, Fla.	56
8/15/73	Gardinier Industries ore, East Tampa, Fla.	47
2/13/73	WHW8 ore (Unidentified EPA Reg. VI sample)	60
8/22/72	Olin Corp. ore (Florida rock) Pasadena, Texas	48 (2)
3/08/73	Simplot ore, Pocatello, Idaho	33
3/08/73	FMC ore, Pocatello, Idaho	30
10/17/73	Texasgulf Lee Creek, N.C. raw ore	17
10/17/73	Texasgulf Lee Creek, N.C. calcined ore	18
	Solid Samples, By-Product Gypsum	pCi/g
8/30/72	Olin Corp. new gypsum pile, Pasadena, Texas	17 (2)
8/30/72	Olin Corp. old gypsum pile, Pasadena, Texas	11 (2)
3/08/73	Simplot, Pocatello, Idaho	16
8/13/73	Agrico, So. Pierce, Fla.	25,24
8/14/73	Royster, Mulberry, Fla.	23,27
8/14/73	Amer. Cyanamid abandoned pile, Brewster, Fla.	28,31
8/14/73	C F Industries, Mulberry, Fla.	21,23
8/15/73	Gardinier Industries, East Tampa, Fla.	21,28
10/18/73	Texasgulf Lee Creek, N.C. gypsum pile	13
10/18/73	Texasgulf Lee Creek, N.C. gypsum filter	14
	Liquid Samples, Streams and Wells	pCi/l
8/12/73	Peace River at Bowling Green, Fla.	6.2
8/15/73	Alafia River south of Plant City, Fla.	0.24
8/14/73	Well at trailer house near USS Ft. Meade, Fla.	8.1
8/29/72	Houston Ship Channel, Olin Corp. intake	0.4 (1)
10/18/73	Pamlico River east of Indian Island, N.C.	0.18
10/18/73	Pamlico River off Pamlico Beach, N.C.	0.17
10/18/73	Pamlico River off Gum Point, N.C.	0.15
10/18/73	Pamlico River off Core Point, N.C.	0.16
10/18/73	Pamlico River off Texasgulf barge slip	0.24
10/19/73	Albemarle River at Rt. 32 Bridge	0.07

TABLE 2 (Cont.)

RESULTS OF RADIUM ANALYSIS
PHOSPHATE MINING AND MILLING AREA SAMPLES

Date	Location	Radium Concentration
	Liquid Samples, Fertilizer Plants	pCi/l
8/13/73	Agrico So. Pierce, Fla. chemical plant gypsum water	92
8/14/73	Royster gypsum water, Mulberry, Fla.	97
8/14/73	Royster seepage from gypsum pile, Mulberry, Fla.	8.8
8/14/73	Royster raw phosphoric acid, Mulberry, Fla.	21
	Olin Corp., Pasadena, Texas	
8/29/72	Gypsum water	56 (1)
8/22/72	Outfall E + F (2 samples)	0.4 to 12 (1)
8/22-29/72	Outfall A (Range of 4 samples)	0.3 to 2.0 (1)
8/22/72	Outfall C	0.2 (1)
	Unknown mill, Sampled by EPA, Region VI	
2/13/73	Sample UMW9	32.7 (1)
2/13/73	Sample UMW10	0.5 (1)
2/13/73	Sample UMW11	31.8 (1)
8/14/73	C F Industries gypsum water, Fla.	91
8/14/73	C F Industries experimental treatment of gypsum water	0.04
8/14/73	Seepage off abandoned Cyanamid gypsum pile	12
	Gardinier Industries, East Tampa, Fla.	
8/15/73	Gypsum water before liming	65
8/15/73	Gypsum water after liming	7.6
8/15/73	Barometric condensers No. 1 and 2	18
8/15/73	Barometric condensers No. 3	0.45
3/08/73	Simplot outfall 001, Pocatello, Idaho	0.14
3/08/73	Simplot outfall 002, Pocatello, Idaho	0.58
3/08/73	FMC, Pocatello, Idaho	0.06
10/16-18/73	Texasgulf Lee Creek, N.C. main outfall	0.19 to 0.26
10/17/73	Texasgulf Lee Creek, N.C. gypsum water	49

(1) Analysis by EPA, Water Planning and Standards, Cincinnati, Ohio.
(2) Analysis by EPA, NERC-Las Vegas.

low in dissolved radium-226, generally between 1 and 2 pCi/l. Slimes from a Florida mine were found to contain 44 pCi/g, or approximately the same concentration of radium-226 in the solid material as in the concentrated ore (48 pCi/g). These results indicate that failure of a slime pond, with subsequent release of slimes to receiving waters, may constitute, in addition to other deleterious effects, a major source of radiochemical pollution to surface waters.

A water sample (Table 2) from the Peace River at Bowling Green, Florida was found to contain 6.2 pCi/l of radium-226: this is over twice the PHS Drinking Water Standard. The Peace River was flooding at the time of sample collection. A portion of the dissolved radium in the river may be the result of leaching many tons of slimes that have been deposited in the river due to slime pond failure. Over the years, many thousands of tons of slimes have entered the Peace and Alafia Rivers and their estuaries through slime-pond failures.

The North Carolina mining operation decants clarified water off the slime pond for discharge to the surface water. A sample of this decant was found to contain over 34 pCi/l (Table 2), which exceeds the concentration permitted by the AEC for discharge to an unrestricted area. This high concentration and extremely high flow yield a radium load of 1.4 mCi/day. This load is greater than the radium load discharged by any uranium mill prior to control of radiochemical pollution in the Colorado River Basin. Radium concentrations in the Pamlico River (Table 2) near the Texasgulf Lee Creek mine and mill were found to be approximately 2.5 times the level in the Albemarle River, a

similar stream north of the mill. Published data (Spalding, 1972) indicate uranium concentrations in Pamlico Sound that were higher than normal background levels. Portions of Pamlico Sound are an approved shellfish harvest area. A single sample of crab meat taken from Pamlico Sound had less than detectable concentrations of radium.

No sampling was conducted in the Tennessee mining area. The Western fields in Idaho and Montana are mined by dry methods and hence use little water in mining processes. The area is rather low in rainfall, with the result that there is little surface water flow. Under these circumstances, it is not expected that runoff from the mine areas other than the slime pond would constitute a majorproblem of radiochemical pollution.

Milling

Published information and results of WPIC-D sampling indicate that the largest component of radiochemical discharges to the water environment associated with the phosphate industry is from the wet-process acidulation step. The sampling to date has shown that this acidulation is responsible for major radiochemical water pollution and the generation of massive amounts of solid wastes that contain radioactive material in a readily leachable form.

Gypsum slurry transport water in mills using Florida phosphate rock is extremely acidic, with a pH less than 2 and was found to contain radium concentrations of over 50 pCi/l for once-through gypsum transport water, and 90 to 100 pCi/l for plants practicing recycling [Figure 4

and Table 2]. Examples include:

	pCi/l
Agrico, So. Pierce (recycle)	92
Royster, Mulberry (recycle)	97
C F Industries, Bartow (recycle)	91
Gardinier, East Tampa (once-thru)	65

The AEC standard (10 CFR 20, 1960) for radium concentrations in unrestricted areas is 30 pCi/l. Gypsum slurry transport water is not normally discharged during dry weather conditions. However, as noted previously, numerous occasions of slurry water discharge occur during wet weather periods. Certain mills throughout the country that use Florida phosphate rock presently discharge slurry water continuously.

In most of the Florida mills, decant from the gypsum piles is conveyed to a pond, generally constructed in a mined-out area, for recycle to the mill. The bottom of such ponds consists of an artesian limestone aquifer which, in turn, overlies the Floridian aquifer. Reaction between the acidic gypsum transport water and the limestone aquifer, together with solution cavities in the aquifer, has resulted in the movement of highly radioactive water into the shallow ground water of a large portion of Polk Country, Florida. The first indication of this was obtained in 1966 during sampling by the Public Health Service, Cincinnati, Ohio. A draft report (Appendix B) indicated that values of up to 79 pCi/l occur in the shallow ground water in the vicinity of the gypsum ponds. Sampling during the course of the WPIC-D reconnaissance investigation, together with the PHS report, indicate that radium concentrations in the shallow wells throughout much of Polk County are greatly in excess of the PHS Drinking Water Standards (1962).

Polk County is the high pressure point on the piezometric map of the Floridian aquifer for peninsular Florida. Thus, radioactive ground water will move radially in all directions in the Floridian aquifer from the Polk County mining and milling site. No towns are known to use water exceeding the Drinking Water Standard for radium, although several supplies, including those of Arcadia and Lake Alfred, approach the value. However, numerous individual and industrial supply wells (Table IV, Appendix B) have been found to contain radium values three to twenty-five times the Drinking Water Standard (PHS, 1962). Insufficient data exist to define the exact area of contamination. It appears that the safety of water in the shallow artesian aquifer in the areas of Range 23 East through Range 25 East, Townships 29 South through 32 South, Polk County should be further evaluated with respect to radium concentration. This is an area of over 1,000 square kilometers (400 square miles). The domestic supply of an estimated 10,000 persons is obtained from shallow aquifers in this area.

At the time of sampling (August 1973), the Gardinier (Cities Service) plant at East Tampa was discharging single-limed gypsum pond water and tailwater from the barometric condensers. The plant is working to recycle both the pond water and the tailwater from the first two condensers. The tailwaters from Condensers No. 1 and 2 contain radium concentrations of 18 pCi/l and should not be discharged. Tailwater from the third-stage condenser contained 0.45 pCi/l radium and will continue to be discharged to Hillsborough Bay. The data (Table 2) indicate that single-stage liming practiced by the plant reduces the

radium concentration in the gypsum pond water from 65 to 7.6 pCi/l, which is still greater than desired levels.

At the Texasgulf Lee Creek mill in North Carolina, samples of the gypsum pond slurry water had radium concentrations of 49 pCi/l (Table 2). The slurry transport water is completely recycled and there is no surface discharge to any receiving water. Other effluents composed primarily of barometric condenser discharge and mine dewatering pumpage contain radium concentrations of 0.19 to 0.26 pCi/l. These concentations are well below any published guidelines or standards. Therefore, it appears that radiochemical pollution in the receiving waters of Pamlico Sound result almost exclusively from slime pond decanting rather than any effluents from the milling process.

As previously noted, the Allied Chemical, Freeport Chemical and National Phosphate plants in Louisiana discharge gypsum slurries containing the by-product material directly to the Mississippi River without impoundment. Liquid samples taken from one of these mills, presently unidentified, indicated dissolved radium concentrations of 32.7 picocuries per liter and 31.8 picocuries per liter (Table 2). In addition, both samples contained extremely high concentrations of radium-bearing suspended solids. Since specific data were not available at the time of publication of this report, the exact location of the sampling point is not known. It should be noted that the discharges from the three Louisiana plants are upstream of the New Orleans water-supply intake. Present EPA STORET files do not contain information on radium concentrations in the New Orleans water supply.

Sampling at the Olin Corp. plant outfalls at Pasadena, Texas, on the Houston Ship Channel, showed radium concentrations generally within the limits specified in various guidelines. However, one individual sample was as high as 12 pCi/l (Table 2). Gypsum pond water, which is discharged only during heavy rain storms, contained a radium concentration of 56 pCi/l. This value is nearly twice the allowable concentration of 30 pCi/l permitted by the AEC for release to an unrestricted area (10 CFR 20, 1960).

Wastes discharged to the Houston Ship Channel eventually reach Galveston Bay, parts of which are approved for commercial harvesting of shellfish. Two samples of shellfish meat collected in Galveston Bay, in February 1973, showed radium concentrations of 18 and 35 pCi/kg. These levels are not considered to be significant concentrations for dietary intake.

As previously noted, the wet-process for phosphoric acid production generates a vast quantity, almost 25 million metric tons per year, of impure gypsum. This is approximately the amount of concentrate acidulated, and five times the phosphorus pentoxide (P_2O_5) produced. Major interest has been expressed in the use of by-product gypsum for construction material manufacture. Due to the wide-spread occurrence of pure deposits of gypsum and the relatively low-cost of storage space available at U. S. plants, no use of the gypsum has been made in the United States. However, such storage is not available at most of the European or Japanese plants, and the by-product gypsum has been incorporated in an inferior grade of gypsum wallboard. Currently, the

U. S. Bureau of Mines is conducting a major investigation into the use of by-product gypsum.

Samples of by-product gypsum were obtained from plants in Texas, Florida, Idaho, and North Carolina. Virtually all the gypsum samples examined (Table 2) were found to contain between 15 and 30 pCi/g of radium as listed below:

	pCi/g
Olin Corp. new gypsum pile, Pasadena, Texas	17
Olin Corp. old gypsum pile, Pasadena, Texas	11
Simplot, Pocatello, Idaho	16
Agrico, So. Pierce, Fla.	25,24
Royster, Mulberry, Fla.	23,27
American Cyanamid, abandoned gypsum pile, Brewster, Fla.	28,31
C F Industries, Mulberry, Fla.	21,23
Gardinier Industries, East Tampa, Fla.	21,28
Texasgulf Lee Creek, N.C. gypsum pile	13
Texasgulf Lee Creek, N.C. gypsum filter	14

This is consistent with published data (O'Riordan, et al, 1972) which indicate radium concentrations of 25 pCi/g in gypsum produced at English mills. This study concludes that inhabitants of a house constructed using wallboard made from by-product gypsum would receive one-tenth the radon daughter exposure level considered safe for uranium miners, assuming an air change within the house occurred every hour. Indications are that the rate of air change in private housing is much less frequent than once each hour. Longer periods between a complete air change would, of course, increase the radon daughter exposure. In the U. S. such exposure would be in conflict with the Federal Radiation Council policy.

By-product gypsum is a relatively water soluble precipitate. Sampling of seepage from an inactive gypsum pile shows that they continue to yield

significant quantities of radium to surface streams and ground water for years after the pile is abandoned. Because of the solubility of the gypsum this problem is analogous to, but more critical than, the problem of stabilization of uranium mill tailings.

Sampling conducted by the AEC and the Idaho Department of Health (AEC, 1970) indicated that gross alpha concentrations in ambient air at Pocatello, Idaho were approximately 15 times background values. Concentrations of polonium-210 (a radon daughter product) in Pocatello were approximately 100 times background values. The AEC conducted limited in-plant sampling in a thermal and a wet-process plant within the city of Pocatello. The AEC concluded that approximately 9.8 Ci/yr of polonium-210 were released to the atmosphere from the two plants. At the FMC thermal plant concentrations of polonium-210 were as high as 41.4 percent of the AEC limit while thorium concentrations of 3.25 times the limit were reported from the J. R. Simplot Co. wet-process plant. EPA is presently conducting mass balance studies within both of these facilities to determine the magnitude and extent of possible radiation problems.

EPA, Region VIII, (Lammering, 1972) has conducted a preliminary mass balance of radiochemical material (polonium-210) primarily related to air emissions from the Rocky Mountain Phosphate Plant at Garrison, Montana. The plant processes animal feed supplements. The Regional study tentatively concluded that approximately 10 percent of the incoming polonium was released to the ambient atmosphere from the plant stacks.

Thermoluminescent dosimentry (TLD) sampling by MFIC-D at two Florida wet-process plants indicated that the radon-daughter concentrations were very low within the plants. Sampling locations did not include the plant stacks. Particulate analysis for polonium-210 was not completed at the time of this report.

V. TREATMENT TECHNOLOGY

WATER

Generally, the industry practice is to recycle water from the gypsum pile for transport of gypsum from the pan filter and for use in scrubbers and condensers. This contaminated water is the main wastewater stream in phosphoric acid plants. During long periods of wet weather many mills find it necessary to discharge excess contaminated water to the receiving streams.

The treatment practice now under consideration as best practicable technology by EPA consists of "double liming" of the excess gypsum pond water before discharge. This procedure assumes the construction and proper operation of a gypsum pile and recycle pond, with excess precipitation as the only discharge.

The "double liming" process [Figure 5] is a two-stage lime neutralization, with an end-point pH in the alkaline range. The treatment is designed to precipitate fluoride and phosphate as calcium fluoride and dicalcium phosphate, respectively. Geochemical literature, uranium-milling experience and limited sampling indicate that "double liming" to a pH greater than eight, while not specifically designed for radium removal, will reduce radium to acceptable levels.

Two separate technologies exist to ensure that the gypsum pond circuit achieves a negative water balance - that is, that gypsum pond water is consumed, eliminating the need for any discharge. This is accomplished by use of contaminated gypsum-pond water for sulfuric-acid dilution, a consumptive use [Figure 4]. Such usage has the advantage

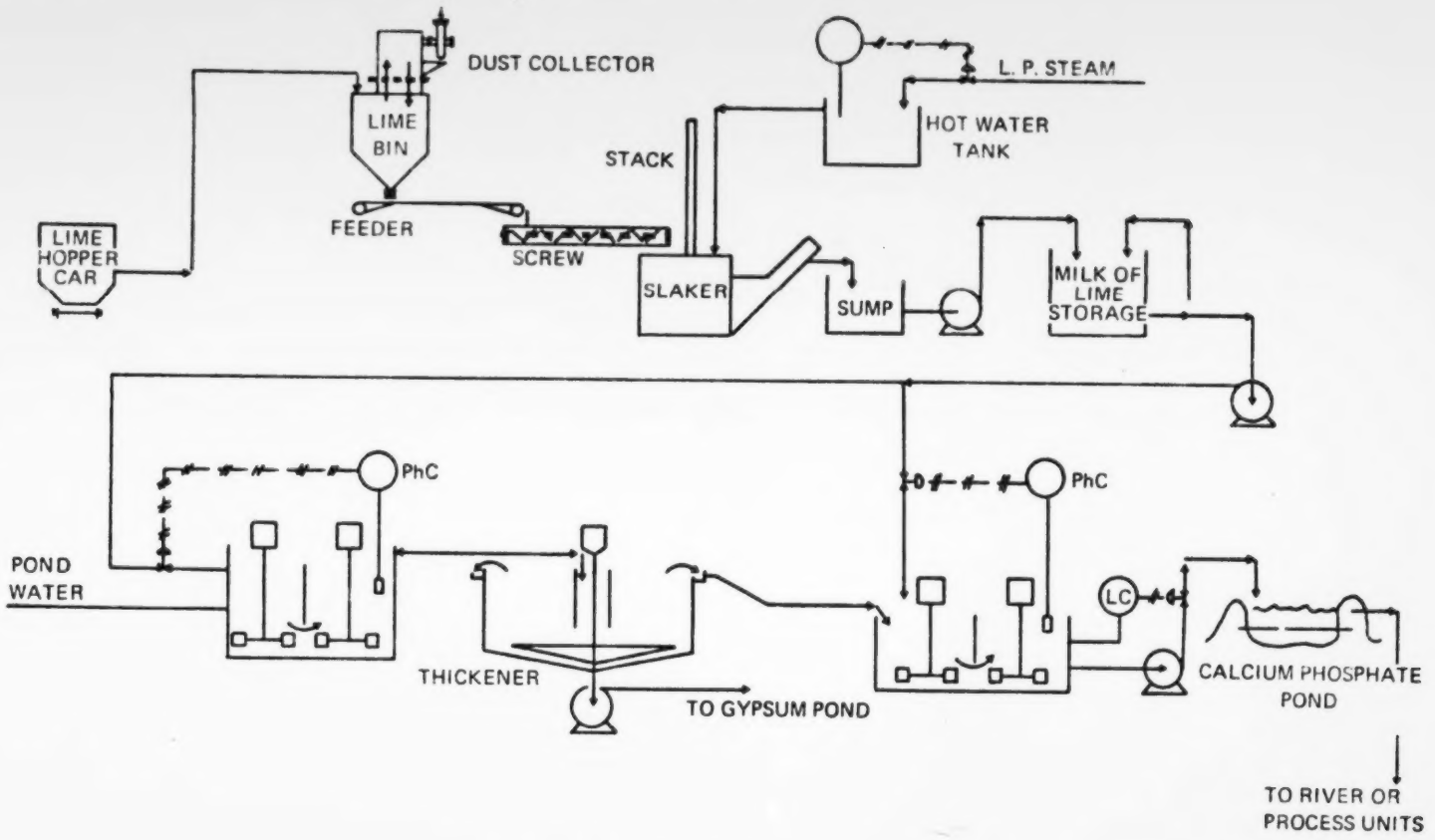

Figure 5. Flowsheet, "Double Liming" Treatment of Gypsum Pond Water (EPA, NOV. 1973)

of recovering additional phosphate that would otherwise be lost to the gypsum pile.

"Both methods of accomplishing sulfuric acid dilution with pond water are proprietary. One method is considered a trade secret. The other is protected by patent. Either process can be added to existent plants or included in the design of a new facility.

The trade secret procedure involves two points. One is the mechanical means by which the dilution is made so as not to create a pluggage problem. The second involves redesign of the phosphoric acid reactor cooling system to remove the heat load formerly removed by the sulfuric acid dilution cooler.

The patented process was developed and has been placed in commercial operation.

It involves sulfuric acid dilution by a two-step procedure in a manner radically different from current practice. The details of process control, vessel design, and materials construction are all proprietary information" (EPA, 1973).

Many plants, especially those in Florida, are located on areas that are underlain by limestone. The acidic gypsum pond water can react with limestone resulting in the development or enlargement of cracks, caverns, and other solution features. This, in turn, permits the movement of contaminated water into the ground water. Many plants which report a negative water balance on the contaminated-water system are actually discharging radioactive waste waters to aquifers.

Solution features located in the bottom of several water-storage reservoirs have been filled with an impervious clay material to eliminat water loss to the aquifer. A wealth of experience has been developed in other fields in the construction of impervious liners for ponds, using material such as clay, plastic, or rubber. These methods are directly applicable to the lining of gypsum ponds.

AIR (EPA, 1972)

Air pollutants from phosphate mining and milling will arise from

rock processing, phosphoric acid production and from fertilizer manufacture. Particulates generally arise from the mining, bulk handling, benefication and product materials, while gaseous pollutants, particularly the fluorine compounds and sulfur and nitrogen oxides, evolve from the acidulation and curing processes.

Little air pollution would be expected during the initial mining and benefication processes where the ore is transported as a slurry. However, subsequent drying and grinding can result in a major source of particulate emissions. Gaseous radioisotopes would also be expected to be driven off during drying. The following emission factors for particulates have been estimated for this phase of the process:

Process	Uncontrolled Emission kg/metric ton	(lb/ton)	Control	Efficiency
Drying	7.5	(15)	Dry cyclone and wet scrubbers	95-99%
Grinding	10	(20)	Dry cyclone and fabric filter	99.5-99.9%
Transfer and storage	1	(2)	Dry cyclone and fabric filter	99.5-99.9%
Open storage piles	20	(40)	---	---

After grinding, phosphoric acid is produced either by the wet or thermal process. In the wet process the major air pollutants are silicon tetrafluoride and hydrogen fluoride. These may continue to emanate from the gypsum ponds containing the process wastes in significant quantities. In the thermal process the major air contaminant is phosphorus pentoxide, P_2O_5, as an acid mist in the absorber tail gas. Since the acid mist

collection system is an integral part of the thermal process, emissions below include this factor:

		Emissions				
		Fluoride		Particulate		
Process	Source	kg/metric ton	(lb/ton)	kg/metric ton	(lb/ton)	Control
Wet	Reactor	9	(18)	-	-	Wet Scrubber
	Gypsum Pond	0.5	(1)	-	-	-
	Condenser	10	(20)	-	-	Wet Scrubber
Thermal	Tower	-	-	2.3	(4.6)	Packed Tower
	Tower	-	-	2.8	(5.6)	Venturi Scrubber
	Tower	-	-	0.9	(1.8)	Electro-static Precipi-tator
	Tower	-	-	0.1-1.5	(0.2-3.0)	Mist Eliminator

In the final phase of the process resulting in the phosphate fertilizer product both fluorides and particulates may be expected as indicated below:

		Emission*				
		Particulates		Fluorides		
Product	Process	kg/ metric ton	(lb/ton)	kg/ metric ton	(lb/ton)	Control
Normal super-phosphate	Grinding, drying	4.5	(9)	-	-	Fabric filters
	Main Stack	-	-	0.08	(0.15)	
Triple super-phosphate	Run-of-pile	-	-	0.02	(0.03)	
	Granular	-	-	0.05	(0.10)	Cyclones and wet scrubbers or fabric filters

* Following control devices.

These emissions result from granulating, screening and bagging of the product.

The efficiency of air pollution control devices given above would not necessarily apply to the radon daughter products since in many cases these particles may be smaller than the particle size distribution for which the equipment was developed. In addition use of radium-containing gypsum transport water for wet scrubbers may result in the presence of equilibrium concentrations of radon in this water.

SOLIDS

The large piles of by-product gypsum in the vicinity of wet-process plants continue to serve as sources of radium for years after the time of abandonment as a result of wind and water erosion. Technologies are available to stabilize this material and eliminate this source of radium pollution (FWPCA, 1966). As a minimum, an adequate program of gypsum-pile stabilization would consist of (1) grading to prevent ponding and promote runoff, (2) sealing with any of a number of chemical sealants to prevent infiltration, and (3) covering with soil to prevent erosion and promote plant growth.

Fertilizer products have been found (Spalding, 1972) to contain most of the uranium present in the phosphate rock. During 1972, almost half as much uranium was present in fertilizer spread on fields as was mined for uranium recovery. Solvent-extraction methods have been proven (Kennedy, 1967) for recovery of uranium from phosphoric acid. Installation of such equipment would eliminate the discharge of uranium to the environment, and increase the nation's supply of uranium,

a resource expected to be in short supply in the next decade (Finch, et al, 1973).

The uranium-recovery techniques would not influence the amount of radium present in the fertilizer product. While most of the radium precipitates with the by-product gypsum, a portion of the radium is present in the fertilizer applied to the nation's lawns and fields. This is estimated to amount to as much as 500 Ci/yr of radium. No practical technology is known for the removal of radium from phosphoric acid or phosphate fertilizers.

VI. SUMMARY AND CONCLUSIONS

As a result of reconnaissance studies conducted from August to November 1973 and summarization and interpretation of previous monitoring data, it can be shown that the mining and milling of phosphate rock for phosphorous and phosphatic fertilizers constitutes an important source of radium being discharged to the environment. Numerous guidelines and standards for protection against radiation are exceeded by these radium-bearing effluents.

Specific findings of this reconnaissance study include:

(1) A major source of radium contamination to the water environment results from the wet-process acidulation step used in phosphate milling. At least 35 plants use this process in the manufacture of phosphate fertilizer. Water contained in the recirculating gypsum slurry systems is radioactive [e.g., 60 - 100 picocuries per liter (pCi/l)] exceeding by at least two to three times the Atomic Energy Commission (AEC) standards for discharge to an unrestricted environment. These waters, at most plants, are discharged as overflow during extended periods of wet weather. However, at three plants (National Phosphate, Allied Chemical, and Freeport Chemical) in Louisiana, no holding systems are reported to be employed and there is a continuous discharge of gypsum slurry to the Mississippi River. These plants are located upstream of the point of intake for the New Orleans water supply.

(2) Samples of ground water collected during 1966 and 1973 in the Central Florida mining and milling area showed radium concentrations in shallow aquifers as high as 79 pCi/l. These aquifers are used for individual water supplies. The limit recommended by the U. S. Public Health Service for radium-226 in drinking water is 3 pCi/l. The AEC standard for release of radium-226 to an unrestricted environment is 30 pCi/l.

(3) Mining of the phosphate rock in Florida does not result in significant discharge of radium to the water environment except that slime pond breaks can result in a massive release of soluble radium. However, at the Texasgulf Lee Creek Mine near Aurora, North Carolina decant water from the slime pond is discharged directly to the Pamlico River. A sample of this water contained a radium-226 concentration of 34 pCi/l. This value exceeds the AEC standard for discharge to an unrestricted environment. At the present flow of decant water from this mining operation, it is calculated that more than 1.0 millicurie per day of radium-226 is discharged to the Pamlico River.

(4) A review of available data indicates that significant quantities of radon gas and its decay products are emitted in the thermal process of phosphorus manufacturing. At least 10 plants in the United States use this process. The majority of these plants are located in Tennessee, Florida, and Idaho. At Pocatello, Idaho, samples collected in 1970 showed that 9.8

curies per year of polonium-210 were being discharged to the ambient atmosphere. EPA is presently conducting total emission studies at this location to determine whether hazardous conditions exist. The effluent guidelines now under consideration by EPA for waterborne effluents from thermal processing installations recommend zero discharge.

(5) By-product gypsum piles contain thousands of curies of radium-226 in a readily leachable form. This material will continue to be a source of radiochemical pollution unless adequate control measures are instituted. Control measures involving stabilization of these gypsum piles are practicable.

(6) Treatment technology, which will control other contaminants such as fluoride and phosphorous, is available and will reduce radium-226 from gypsum transport water to acceptable levels. This technique involves the "double-liming" procedure. This is the recommended technology now being considered by EPA as the best pacticable for this industry. Alternative control measures permit the development of a negative water balance within the plant to eliminate the need for any surface discharge.

(7) Treatment technology now being employed to control air pollution from phosphate mills may control emissions of radon gas and its daughter products from thermal processing plants. However, definitive results await the outcome of the ongoing EPA sampling effort. At plants using the wet-process acidulation step of manufacturing phosphate fertilizer, wet scrubber technology

may not adequately control emissions of radon gas and its daughter products since the scrubbers are fed with gypsum transport water which already contains high concentrations of radium-226. The extent of this problem has not been measured at this time.

(8) Present practice in Europe and Japan utilizes by-product gypsum in the manufacture of an inferior grade of wallboard, used in building construction. This wallboard exposes inhabtants to increased concentrations of radon and its daughter products. Research is underway which can be expected to lead to similar uses in the United States. This practice would increase the radiation exposure of the general public and, as such, would be contrary to Federal Radiation Council policy.

(9) The International Commission on Radiological Protection, the National Committee on Radiation Protection, and the Federal Radiation Council proposals for radiation exposure protection are "recommended guidelines." The only enforceable radiation standards are those promulgated as a regulatory statute by the AEC (10CFR 20). The statute applys only to AEC licensees. The use of radioactive material, or other sources of radiation not licensed by the Commission, is not subject to the regulation. The enforceability of any radiation guidelines or standards as related to the phosphate industry is questionable.

VII. RECOMMENDATIONS

It is recommended that:

(1) The proposed treatment technology in the effluent guidelines now under consideration by EPA for the Basic Fertilizer Chemicals Segment of the Fertilizer manufacturers Point Source Category be implemented at the earliest possible time through the National Pollution Discharge Elimination System [These guidelines were proposed in the Federal Register of December 7, 1973]:

(2) Waste discharge permits issued to plants in this category require that no plant discharge gypsum or untreated process water to surface streams:

(3) Treated process water discharged from phosphate fertilizer manufacturing installations be limited to 3 pCi/l of radium-226 to take effect no later than July 1, 1977 as this level is achieveable through implementation of practicable and demonstrated treatment technology presently employed by the industry:

(4) All new plants be designed to eliminate the need for process-water discharge, and all plants should implement process modifications to eliminate process-water discharges as soon as practicable and in no case later than July 1, 1983;

(5) The EPA immediately initiate an investigation to determine the magnitude and effect of radium-226 in seepage of contaminated water from gypsum ponds, and where these investigations indicate substantial seepage of water containing radium-226 to aquifers,

control measures, including lining of ponds with impermeable substances, shall be instituted, with new plants employing lining of gypsum ponds when dictated by geologic conditions;

(6) Regulations be promulgated to ensure that (a) all precipitates from process-water treatment systems are placed on gypsum piles, (b) upon abandonment, gypsum piles are stabilized to prevent future leaching or erosion, (c) as a minimum, such stabilization include grading to promote runoff and prevent ponding, sealing to prevent infiltration, and covering with soil to permit vegetative stabilization, and (d) by-product gypsum be prohibited for use as a construction material in confined areas;

(7) The prevalence of use of ground water containing radium concentrations exceeding the PHS drinking water standards resulting from phosphate manufacture be ascertained through appropriate investigative procedures;

(8) Ambient and stack sampling for radon gas and its daughter products be expanded to include wet process phosphoric acid plants in addition to the present EPA sampling of thermal process plants, and treatment technology be evaluated to determine removal efficiency of radon gas and its decay products; and

(9) To ascertain the possible hazard to the general public from continuous exposure to emissions of radium and its decay products as a result of phosphate manufacturing, an investigation be undertaken to evaluate the total dietary uptake of radium in persons living in areas known to be influenced by phosphate manufacturing.

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APPENDIX A

ANALYTICAL METHODS AND QUALITY CONTROL

ANALYTICAL METHODS AND QUALITY CONTROL

The methods used at EFIC-D in analyzing the samples collected for this report were developed to overcome the analytical interference caused by excessive amounts of sulfate in the water and solid samples, and to generally simplify the procedures. Historically, several precipitations were used to remove isotopic interferences so that samples could be counted, using planchet-counting equipment. The radon emanation technique used by EFIC-D, however, is specific for radon; and when radon samples are held for 3-4 hours before counting only radon-222 is measured. Thus, these methods are specific for the determination of radium-226, the parent of radon-222, and only require the complete dissolution of the sample while in the bubbler.

A. ANALYTICAL QUALITY CONTROL DATA

Replicate standards were analyzed at several levels using the Barium coprecipitation method yielding the following results:

Standard Concentration	Number Samples	Mean	1-Sigma	95% C.L.
Blank	6	0.036	0.025	0.05
0.976 pCi/l	6	0.952	0.045	0.09
9.76 pCi/l	7	8.79	0.61	1.22
39.04 pCi/l	8	35.76	1.004	2.01

The detection limit is defined as twice the background noise (Blank) standard deviation or 0.05 pCi/l for liquid samples.

The above results indicate that in the range of zero to about 20 pCi/l, the confidence level of the measurement is about ±10%. Above 20 pCi/l the 95% confidence level improves to around ±5%. The 95% confidence levels based on counting statistics alone are about 1 - 2 % and thus contribute little to the precision of measurement.

In the various procedures used for the analysis of Radium 226 by radon emanation, the systematic error most likely to occur would be to lose some radium during sample preparation, resulting in the reporting of concentrations lower than true concentrations. At HASL-Denver, standards were added to actual samples resulting in percent recoveries of 100 ± 5%. Admittedly, liquid standard additions to solid samples is not necessarily a valid means of spiking, it is the best that can be done, lacking a solid standard. Solid spike material should match the sample matrix as close as possible and, since solid sample matrices vary so much, a solid spike suitable for a range of solid samples is impossible.

Standard Additions

Sample Type	Sample Conc.	Spike	Response	% Recovery
Solid	51 pCi/g	97.6	149	100.3
Liquid	0.98 pCi/l	0.970	1.99	98.3
Liquid	8.0 pCi/l	9.70	17.9	95.7
Liquid	100 pCi/l	97.6	202	102.2

Replicate analyses of solid as well as liquid samples were performed and results were obtained which were well within the precision of the method. As a further check on the confidence of the methods employed at HEIC-Denver, liquid and solid samples were split with two other EPA laboratories that analyze for radium by the radon emanation technique. These laboratories were the Technical Support Laboratory at HERC Las Vegas, and the EPA Eastern Environmental Radiation Laboratory in Montgomery, Alabama. These results are summarized below:

Replicate Samples

Sample Type	HEIC-Values First	Second	HERC-Las Vegas Values First	Second	Third	EERL First	Values Second
Liquid	92	90 (direct)	-	-	-	94	90
Solid	25	24	-	-	-	-	-
Liquid	97	-	99	110	-	-	-
Solid	48	51	47	54	53	41	47
Solid	23	27	21	27	18	26	-
Liquid	.31	.98	-	-	-	-	-
Liquid	8.1	8.0	-	-	-	-	-
Solid	28	31	-	-	-	-	-
Solid	21	23	-	-	-	-	-
Liquid	91	100	-	-	-	-	-
Solid	21	28	-	-	-	-	-
Liquid	7.6	-	8.1	11	-	-	-

(Units of pCi/l or pCi/g omitted for clarity)

Precision data for these results are not yet available; however, the close agreements are indicative of adequate methods employed by all three laboratories.

3. METHODS

RADIUM-226 IN WATER

(from unpublished USGS method)

Principle:

Dissolved radium in water is co-precipitated with barium sulfate which is then separated by centrifuging. The precipitate is dissolved in alkaline DTPA, and transferred to radon bubbler tubes where ingrown radon is removed by a helium purge.

Radon is allowed to grow in for a measured period of time after which it is transferred to alpha scintillation cells by a second helium purge and counted. Radium-226 concentration in the original sample is calculated based on the radon-222 and daughter product activity making the appropriate corrections for ingrowth and decay.

Reagents: (Use reagent grade chemicals unless otherwise specified.)

1) Barium carrier solution: 50 mg Ba^{++}/ml; dissolve 75.81 g barium chloride (BaCl2) in distilled water and dilute to 1000 mls.
2) Sulfuric acid, concentrated.
3) Sulfuric acid wash solution: add 5 mls of concentrated H_2SO_4 and 3-4 drops of Triton X-100 to 4 liters of distilled water.
4) DTPA-TEA solution: dissolve 10 g of sodium hydroxide pellets in a beaker containing 60 mls of distilled water and stir in cold water bath until dissolved. Add 20 g of purified DTPA and continue stirring until dissolved. Add 17 mls of 50 percent triethanolamine, mix and dilute to 100 mls. Place in a teflon bottle and store in the dark to prevent reagent decomposition and discoloration.

5) Defoaming emulsion: Dow Corning Anti Foam H-10 emulsion; dilute to approximately 4 to 5 percent solution with distilled water before using. Other defoaming agents may be used provided they contribute negligible Radium activity to the samples.

Procedure:

1) Place one liter of water into a 1500 ml beaker. If the sample has not previously been preserved with 5 ml/l concentrated HCl, add 5 ml HCl and stir.
2) Add 1 ml of 50 mg/ml barium carrier (Ba^{++}) to the sample and stir.
3) Cautiously, and while slowly stirring, add 20 mls of concentrated sulfuric acid to each sample (Use of a 500 ml dispensing flask fitted with a 20 ml delivery head facilitates the acid addition.) Stir well after the acid addition. Allow barium sulfate precipitate which forms to settle overnight.
4) Carefully remove the supernate by decantation or suction and quantitatively transfer the balance of the supernate and precipitate to a 40 ml centrifuge tube using a rubber policeman and small quantities of dilute sulfuric acid-aerosol wash solution.
5) Centrifuge as necessary, decant and discard supernate.
6) Add approximately 10 mls of distilled water and 1 ml of DTPA reagent to the precipitate in the centrifuge tube. (More DTPA may be used with samples containing excess sulfate). Disperse the percipitate in each tube by using a wiggle plate mixer or an ultrasonic unit. Place tubes in a wire rack and immerse rack and tubes to a depth of approximately one inch in a boiling water bath.

7) Complete dissolution should occur within a few minutes if the barium sulfate "pellet" was adequately dispersed. Occasionally, total volume in the centrifuge tubes may decrease by 4-5 mls as a result of prolonged heating and the precipitate may not dissolve. Addition of distilled water to bring the total volume to approximately 20 mls (max.) plus additional re-dispersion and heating will usually result in rapid dissolution of even difficultly soluble precipitates. After the precipitate has dissolved, cool the tubes.

8) Using a funnel with a fine tip, transfer the cooled solution to a clean bubbler. Wash the centrifuge tube several times with distilled water and add the washings and sufficient additional water to the bubbler to leave approximately one inch of air space at the top. Add 1-3 drops of defoaming emulsion to the solution in the bubbler to minimize frothing during purging.

9) Attach stopcock and "O" ring to bubbler using clamp, leaving outlet stopcock on bubbler assembly in open position. Attach helium line (3-5 psi) to inlet side of bubbler. Slowly open stopcock on inlet until a stream of fine bubbles rise from the porous disc. Maintain a steady flow of bubbles through the sample for approximately 20 minutes to completely sparge all ingrown radon from the solution, Close inlet stopcock and allow pressure under porous disc to equalize momentarily. Close outlet and record time. (Purge)

10) Use of a magnetic stirring apparatus and small stirring bar in the bubbler assembly results in a mixing of the solution during sparging and a more complete removal of ingrown radon.

11) Allow from 3-14 days ingrowth time for radon-222, (samples suspected of high radium-226 values require shorter periods of ingrowth), depending upon the radium-226 concentration in the original sample, volume of sample used, etc.

12) Subsequent de-emanations: Set up bubbler as in step 9 except outlet stopcock remains in the closed position at all times until sparging assembly is prepared to transfer the radon-222 in bubbler into the scintillation cell. Attach bubbler to drying tube with "O" ring and clamp. Evacuate sparging assembly, including cell, with vacuum pump for approximately 1.5 to 2 minutes. Close stopcock at vacuum pump, turn pump off and momentarily crack "O" ring connection to purge trapped air from line and bubbler inlet connection. Clamp and allow system to stand for approximately 2 minutes. If the system leaks, the manometer meniscus will flatten or the mercury level in the manometer will begin to fall. If the meniscus remains stable proceed as follows.

13) Carefully open bubbler outlet stopcock until manometer begins to fall (check porous disc for fine bubbles). Allow vacuum to equilibrate slowly, (otherwise there is excessive risk of drawing liquid sample into drying tube). Bubbling will slow appreciably in a few seconds. Slowly open outlet stopcock completely. Then continue with sparging by slowly opening bubbler inlet stopcock, checking porous disc carefully for rising bubbles, (<u>flow-rate must be closely controlled again at this point, to prevent</u>

sudden surge of liquid into drying tube.) Allow pressure to build up slowly, controlling manometer fall-rate to complete sparging in 15-20 minutes. Close cell stopcock approximately 4 mm before manometer reaches atmospheric pressure to guard against pressure leak from cell during counting.

14) Close down sparging assembly stopcocks from cell to helium inlet line in sequence as rapidly as possible. Record time. Remove bubbler from assembly quickly and crack outlet stopcock momentarily to release helium pressure. If a re-run is necessary, the bubbler can be de-emanated again after a sufficient ingrowth time has elapsed.

15) Place cell in light-tight counting chamber (or other dark place if counting chambers are not immediately available). Allow 3 to 4 hours for the ingrowth of short lived radon daughters in the cells before counting. Count cells overnight (approximately 1000 minutes.) Counting of high count rate sample (50 cpm) should be terminated at 5-10,000 total counts. All cells should be evacuated and flushed several times to reduce the rate of background increase in the cells. Overnight counting of a high count rate sample may raise a cell background to the point where it is no longer useable for low level determinations. Cell backgrounds should be 0.10 cpm or less. High count rate samples may be accurately calculated at 10,000 total counts, regardless of counting time.

16) Dates, times, counts and all other pertinent sample information should be recorded on data and calculation sheets.

17) Counting cell K-factors are determined as in Standard Methods section 305.4a, 13th edition.

FUSION DECOMPOSITION OF SOLID SAMPLES FOR ^{226}Ra ANALYSIS BY RADON EMANATION (EXPERIMENTAL)

Apparatus:

1) Platinum crucibles (35 ml. capacity) and tongs
2) Fisher (i.e., Meeker type) burner
3) Muffle furnace (900°C. capability)
4) Steam or hot water bath
5) Ultrasonic cleaner
6) Centrifuge and centrifuge tubes (40 ml.)

Reagents:

1) Carbonate-Borate flux: weight ratio of 1 part $Na_2B_4O_7 \cdot 10H_2O$ sodium tetraborate decahydrate to 4 parts Na_2CO_3 sodium carbonate (anhydrous). Mix dry components thoroughly.
2) Ammonium Carbonate (0.5%) wash solution: dissolve approximately 50 gr. of $(NH_4)_2CO_3$ purified powder in de-ionized water. Dilute to one linter.
3) 6N HCl

Procedure:

1) Weigh 4.0 gr. of carbonate-borate flux into 35 ml. platinum crucible.
2) Melt flux over Fisher burner and distribute on walls of crucible, i.e., line the crucible with flux.
3) Weigh sample (up to 1.0 gr.) into tared coated crucible and add 4.0 gr. flux. Mix thoroughly with a stirring rod.

4) Top off crucible with 1.0 gr. flux. Spread over mixture as a "lid."

5) Fuse at 900°C. for 1 hr. in muffle furnace.

6) After cooling, remelt over Fisher Burner and coat crucible walls with melt again.

7) After again cooling, fill crucible with $(NH_4)_2CO_3$ wash solution and allow to stand overnight, preferably over hot water or steam bath. Cover so the sample doesn't evaporate to dryness.

8) Transfer melt into centrifuge tube with $(NH_4)_2CO_3$ wash solution with aid of ultrasonic cleaner to break up the solid pellet.

9) Centrifuge, decant and discard the wash solution. Wash several times. Use ultrasonic bath to break the "pellet" into finest particles possible.

10) After final decantation, dissolve melt in 6N HCl.

11) Transfer solution to "radon bubbler," as in Step 8 "Radium-226 in Water" and continue with steps 9-17.

Additional Comments:

1) The $(NH_4)_2CO_3$ wash is to wash out soluble sulphate salts which would cause Ra-Ca to re-precipitate as sulphates after dissolution of carbonate melt. The Ra-Ca carbonate is insoluble in the wash solution.

2) If there is more than a few percent silica present in a sample it may be necessary to evaporate the sample in a platinum crucible with hydroflouric acid (15 ml per 1.0 gr. sample) before fusion. High silica will cause a gel to form in the dilute hydrochloric acid solution.

3) High sulfate samples (e.g. gypsum) cannot be quantitatively analyzed by this method. Losses from 10% to 30% occur. An alternate method for gypsum analysis for Ra would be to treat a 0.1 - 0.5 gr. sample directly with an excess of sequestering agent used in the "normal" water analysis.

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WET DIGESTION OF BIOLOGICAL SAMPLES FOR ^{226}Ra ANALYSIS BY RADON EMANATION

Apparatus:

1) 100 ml. beakers
2) hot plate

Reagents:

1) concentrated HCl
2) concentrated HNO_3

Procedure:

1) Place 5 gr. of suitably (see comments) ground sample in a 100 ml. beaker. Add 10 ml. of concentrated HNO_3 and evaporate to near dryness; if the residue is not white or very light colored, add more HNO_3 and repeat evaporation.
2) Add 10 ml. of aqua regia (1 part HNO_3 + 3 parts HCl) and evaporate to near dryness. Bring volume to 5 ml. with aqua regia.
3) Wash solution into radon bubbler with de-ionized water, seal and begin ingrowth.

Comments:

1) Dissolution of samples which are particularly resistant may be accelerated by adding (dropwise, slowly and carefully!!) a few milliliters of 30% H_2O_2.
2) Oil drops may appear after dilution of final aqua regia solution with de-ionized water. These may be dispersed with Triton X-100 or some similar detergent/solubilizer. This, of course, causes

quite a bit of foaming during purging and deemanation. Add extra anti-foaming agent and use a slower bubble rate.

3) After transferring the solution to a radon bubbler, the beaker may be heated with 5 ml of de-ionized water and 1 ml of DTPA solution (see "^{226}Ra in water") and rinsed into the bubbler.

4) A sample (e.g., edible portion of oyster) may be prepared by freezing then grinding in a blender with dry ice. The dry ice is then allowed to sublime in a refrigerator.

APPENDIX B

DRAFT REPORT

ON

RADIUM-226 AND RADON-222 CONCENTRATIONS

IN

CENTRAL FLORIDA GROUND WATERS

BY

S. David Shearer

Bradford Smith

D. E. Rushing

Radium-226 and Radon-222 Concentrations in Central Florida Ground Waters

INTRODUCTION

The Physical and Engineering Sciences Section, Technical Advisory and Investigations Branch, FWPCA, was requested by the Florida State Board of Health to assist them in assessing the radium-226 and radon-222 concentrations in central Florida ground waters, especially those areas around the phosphate fertilizer plants.

The phosphate deposits are considered to be a potential low-grade uranium ore, hence, the uranium concentration in the phosphate-bearing formations is much higher than the natural abundance for all rocks. Additionally, all phosphate-ore formations are older than one million years, and since the uranium is considered to be syngenetic, radium is expected to be present in equilibrium amounts with the uranium.

High radium concentrations have been found in both the finished fertilizer and the waste waters in ponds adjacent to the plants. Processing of the phosphate ore is expected to partition the uranium and radium with the radium being concentrated in the waste products and the uranium enriched in the phosphate product. Sampling and analysis have not been made to confirm this supposition. However, disposal of liquid wastes directly to the environment may be an immediate hazard and leaching of solid-waste spoil piles may be a long-term supply of radium pollution.

Ground-water contamination is possible in Polk County and other areas of central Florida. Most of the area is underlain by a surficial cover of thin beds of sands, gravels, clay, and marl of Pliocene to Recent age. Underlying these younger beds is the Bone Valley Formation and the Hawthorn Formation from which it was derived. Both are phosphoric but only the Bone Valley contains commercially minable phosphate ore. The Hawthorn Formation is a confining layer for the artesian water in the "principal artesian aquifer" of central Florida. In this area the top of the aquifer is the Tampa Limestone; this formation and succeeding older formations to as much as 1,500 feet below the land surface produce copious amounts of fresh ground-water. Recharge to the artesian aquifer is in areas north of Polk County where the aquifer beds are at or near the surface. In Polk County local recharge occurs where sinkholes extend from the surface through the Hawthorn Formation to the aquifer. It is through such sinkholes that radium polluted water may enter the artesian aquifer, either by direct discharge into a sinkhole or by surface runoff or subsurface migration to a sinkhole. Radium pollution that has been incorporated in the ground-water phase may be discharged to the marine environment by surface and submarine springs. Many large springs have been noted to the west and north of Polk County on land and off-shore in the Gulf.

During the period January 10 - 21, 1966, a number of ground-water samples were collected in the central Florida area for radiochemical and inorganic chemical analyses. The area covered in this ground-water sampling extended in a north-south direction from Crowland to Arcadia

and in an east-west direction from Kissimmee to Tampa. Samples were collected from the following counties: De Soto, Hardee, Highlands, Hillsborough, Lake, Manatee, Orange, Osceola, Pasco, and Polk. Figure 1 shows the general survey area and sample collection points.

Table I presents a summary of the various types of samples collected and a breakdown of the 80 private wells which were sampled. Of the 105 individual wells sampled, depth was not obtained on 29 of them. Depth of the remaining wells ranged from 15 feet to 1480 feet. Approximately 1350 people were using water from the 80 private wells sampled and 157,300 people were using the municipal wells sampled.

FIELD COLLECTION AND LABORATORY ANALYSIS PROCEDURES

As it was desired to analyze all samples collected for radon-222, special collection procedures were employed to ensure that this isotope remained in solution. This was done in the following manner. The faucet at the well or sampling point was turned on and allowed to run slowly for a short time. A one-quart polyethylene bottle was filled to overflowing, the bottle squeezed slightly while full and a screw cap tightened and sealed with black plastic tape. In this manner a slight negative pressure existed inside the bottle and any leakage was into rather than out of the water, thus ensuring minimum or no loss of radon from the sample. In addition to the one-quart sample, two one-gallon samples were collected at each sampling point. The latter provided sufficient sample for detailed radiochemical and inorganic chemical analyses.

Upon receipt of samples in the laboratory, a volume of approximately 30 ml was transferred from the quarts to a hand evacuated radon

Table I

Summary of Types of Samples Collected

25 Municipal Well Supplies

80 Privately Owned Wells

64 Domestic Use Only

6 Domestic plus Industrial Use

4 Domestic plus Other Uses

2 Domestic plus Irrigation

4 Industrial Use Only

1 Thermal Spring

1 Natural Well

2 River Waters

2 Industrial Waste Waters

bubbler which is shown in Figure 2. The bubbler was then weighed to obtain a volume and the radon subsequently stripped from solution and transferred to an alpha sensitive counting chamber by means of passing aged compressed air through the sample. The scintillation cell and the deemanation assembly are shown in Figures 3 and 4. The remaining water in the one-quart bottle was filtered through 0.5 micron membrane filters, acidified, and placed aside for subsequent radium-226 determination.

A number of the samples were selected for detailed radiochemical and inorganic chemical analyses.

Radon-222 and Radium-226 Concentrations

Table II presents a percentile summary of the radon-222 and

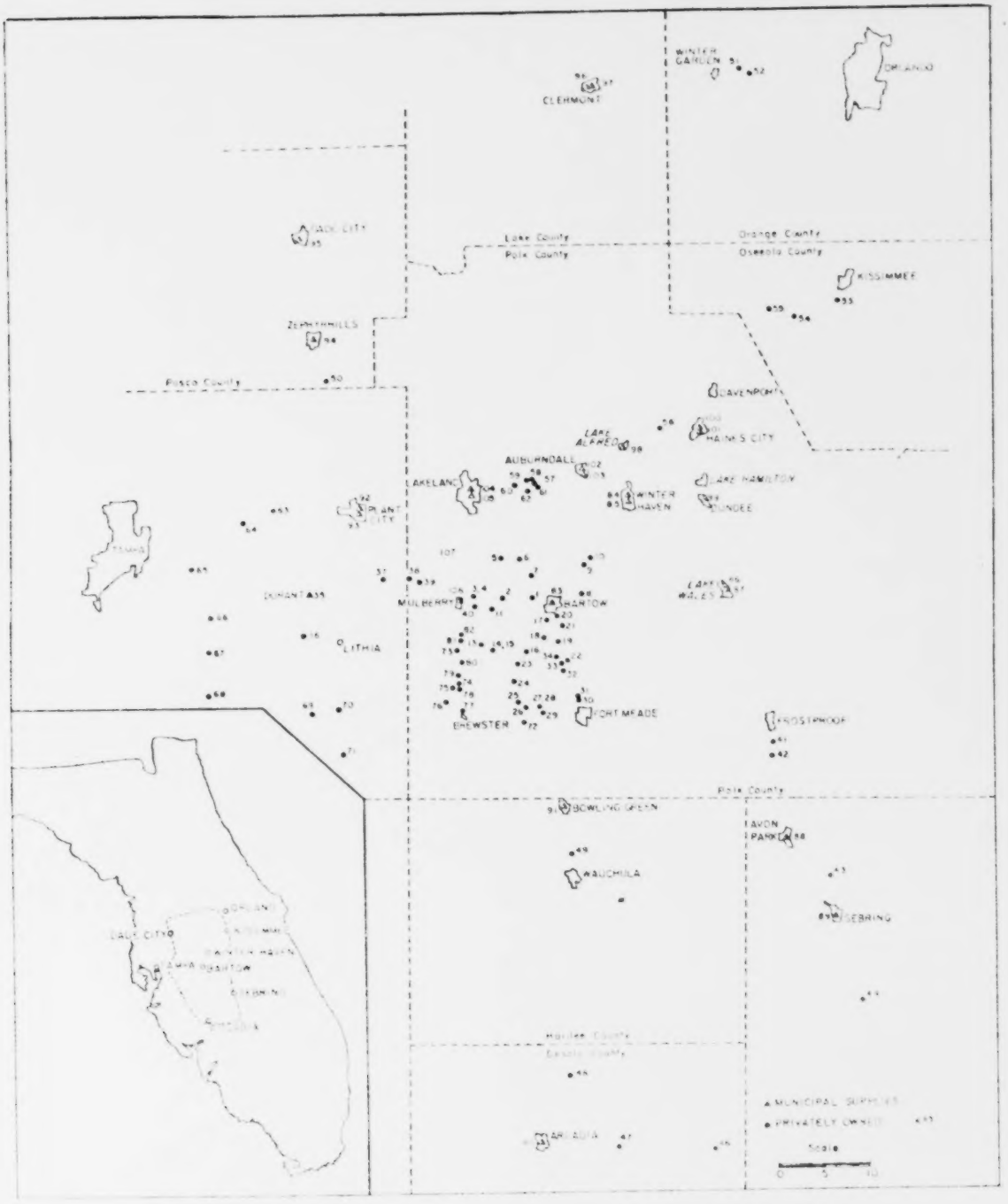

Figure 1 GENERAL SURVEY AREA FLORIDA GROUND WATERS

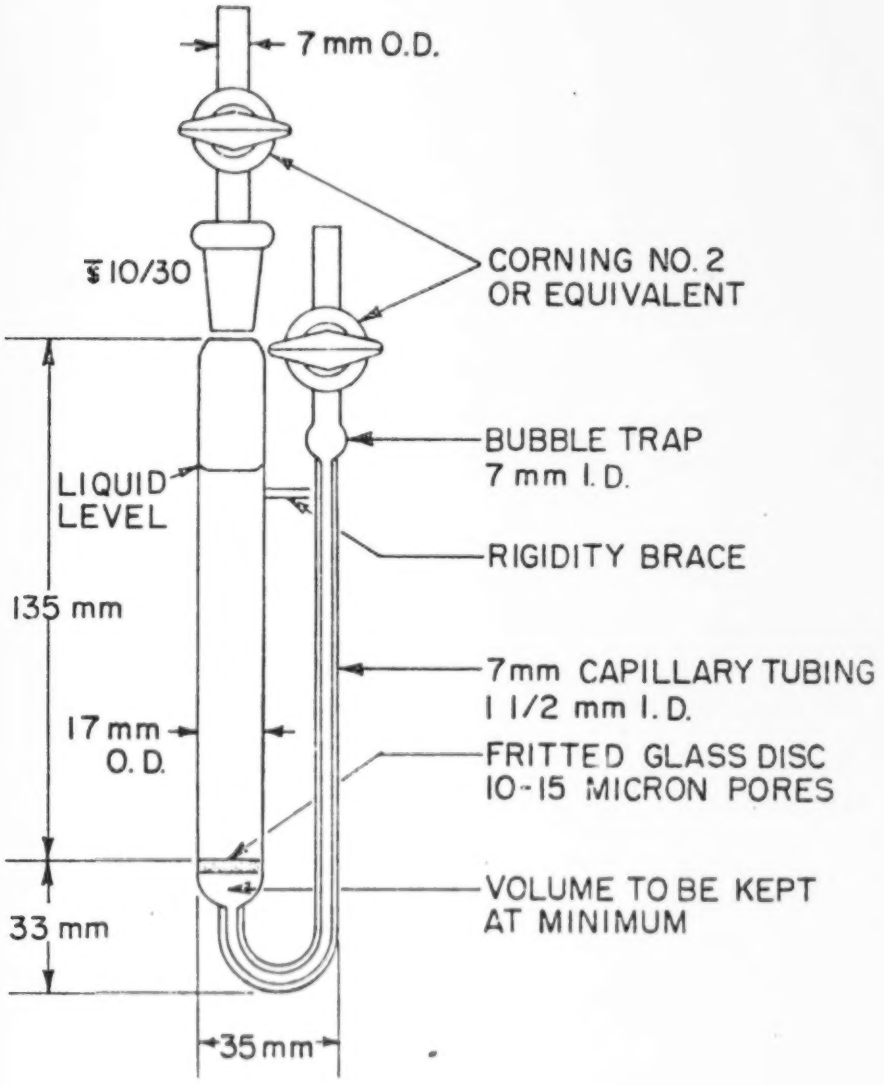

Figure 2. RADON BUBBLER

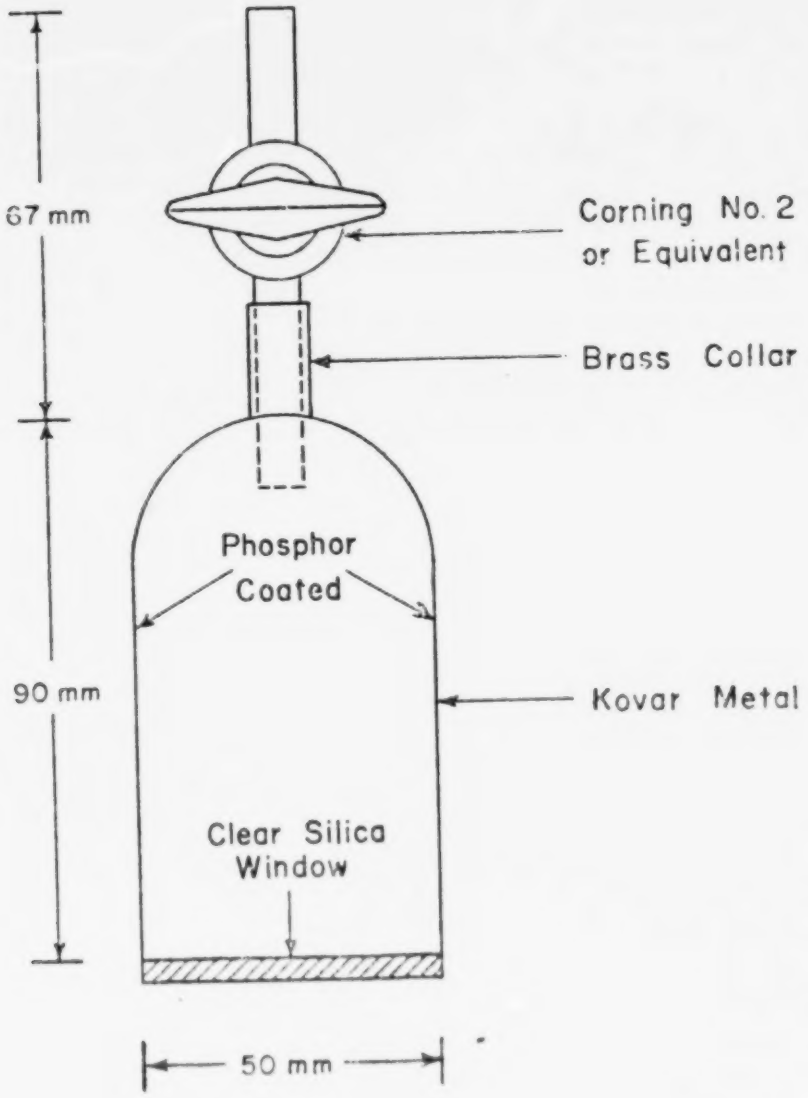

Figure 1. Scintillation Cell

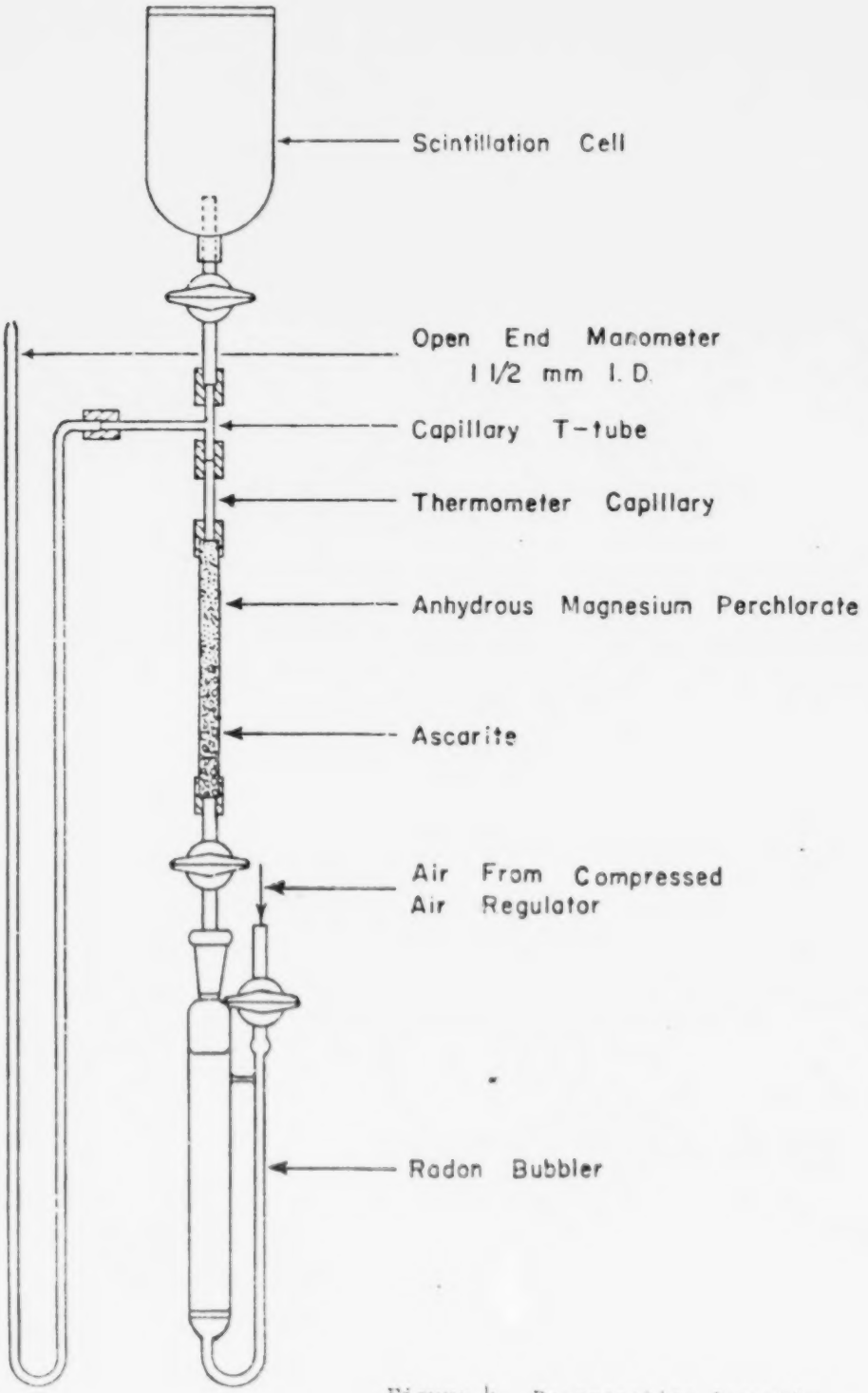

Figure 4. De-emanation Assembly

Table II

Summary of Radon-222 and Radium-226 Concentrations

(pc/l) in Central Florida Ground Waters

105 Drilled Wells	Radon	Radium
90% samples	< 3430	< 4.6
75%	< 4160	< 2.4
50%	< 1860	< 1.2
25%	< 260	< 0.5
RANGE OF CONCENTRATION	23 - 46,600	0.0 - 76
80 Private Wells		
90% samples	< 9460	< 4.6
75%	< 4190	< 3.9
50%	< 2780	< 1.4
25%	< 970	< 0.5
RANGE OF CONCENTRATION	23 - 46,600	0.0 - 76
25 Municipal Wells		
RANGE OF CONCENTRATION	35 - 720	0.0 - 4.1

radium-226 concentrations found in the well water samples. Table III presents a tabulation of municipal well supplies with information on sampling site, depth of well, radon-222, radium-226, uranium, thorium, lead-210, and polonium-210 concentrations. Table IV is a summary of the 80 privately owned wells. Table V is a summary of radon and radium concentrations in several miscellaneous samples which were collected. Tables VI and VII present the inorganic chemical analyses from a selected number of stations for municipal and private water supplies, respectively. All radon-222 concentrations have been corrected to time of sample collection.

Of the 105 well samples collected, 60 privately owned wells were located in the central phosphate valley area. For purposes of this report, this is considered to be the area bounded by Range 22 East (R22E), Range 27 East (R27E), Township 27 South (T27S), and Township 33 South (T33S). The average radon concentration of the 60 samples in this area was 4950 pc/l with a range of 76 to 46,600 pc/l. The average radon concentration for the 20 privately owned wells outside of this area was 1,100 pc/l, with a range of 23 to 3,830 pc/l.

INTERPRETATION OF DATA

The interpretation of the data is limited as the study was first designed as a reconnaissance of the radon and radium concentrations in water supplies in and around the phosphate mining and processing areas. Thus the study was intended to be more heuristic than comprehensive. However, a few conclusions can be drawn from the data with reasonable accuracy.

At first glance of the data, there seems to be no correlation between the radon and radium concentration. Any obvious correlation

Table XII

Municipal Well Supplies - Central Florida

Sample Number	Municipal Supply	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (µg/l)	α Th (pc/l)	Pb-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
83	Barbow Well No. 3 (RAW)	650	260	1.6	-	-	-	-		
	Barbow (Treated) - Aeration, Filtration, Chlorination		80	1.4	-	-	-	-		
84	Winter Haven Wells 1 and 2 (RAW)	1 - 593 2 - 616	20	0.67	-	-	-	-		
85	Winter Haven Wells 3 and 4 (RAW)	3 - 648 4 - 640	95	0.58	1.2	0.12	0.0	0.0	2.7	2.7
86	Lake Wales Well 1, Market Sq. Plant (RAW)	1022	60	0.76	-	-	0.2	0.1	3.3	3.2
87	Lake Wales Well 1, Grove Ave. Plant (RAW)	1063	35	0.47	-	-	-	-		
88	Avon Park (RAW)		560	0.93	0.7	0.11	0.5	0.1	3.7	3.7
89	Sebring Franklin St. Well (RAW)	1430	140	-	0.7	0.11	0.2	0.1	0.4	3.8
90	Arcadia Well 1 (RAW)	495	480	3.3	0.9	0.52	0.6	0.1	4.9	24
	Arcadia (Treated) Aeration, Chlorination		210	2.5	-	-	-	-		

(Continued)

Table III (continued)

Municipal Well Supplies - Central Florida

Sample Number	Municipal Supply	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (ug/l)	α Th (pc/l)	Po-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
91	Bowling Green at Water Tank		260	2.7	0.9	0.15	0.3	0.3	2.4	11
92	Plant City Well 3	750	150	0.77	-	-	-	-		
93	Plant City Well 2	368	360	0.00	1.2	0.06	0.1	0.0		
94	Zephyrhills	425	360	0.31	1.2	0.00	0.3	0.0	2.9	-
95	Dade City Well 1	150	305	0.00	-	-	-	-		
96	Clermont South Well	525	600	0.39	-	-	-	-		
97	Clermont Highland Well	550	720	0.29	1.8	0.04	0.1	0.0	0.8	
98	Lake Alfred Well 4 (RAW)	560	220	4.1	-	-	-	-		
	Lake Alfred (Treated) Aeration, Chlorination		50	1.8	-	-	-	-		
99	Dundee Well at City Park		560	0.0	-	-	0.0	0.0	0.7	4.3
100	Haines City Well 7	800	125	0.74	-	-	-	-		
101	Haines City Well 8	565	115	0.73	-	-	-	-		
102	Auburndale, Tampa St. Well	616	110	0.50	-	-	-	-		
103	Auburndale, Water Tower Well		85	0.53	-	-	-	-		

(continued)

Table III (continued)

Municipal Well Supplies - Central Florida

Sample No.	Municipal Supply	Depth of Well (Ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (µg/l)	α Th (pc/l)	Pb-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
194	Lakeland Well - 9 N. Florida Ave.	865	160	0.80	-	-	0.1	0.1		
195	Lakeland Well 22	821	260	0.84	-	-	-	-		
196	Mulberry Well 1	778	165	0.45	1.4	0.06	0.4	0.1		
197	Mulberry Recreation Center - North of Mulberry		320	0.23	-	-	-	-		

Table 7A

Privately Owned Wells - Central Florida

Sample Number	Location	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (µg/l)	α Th (pc/l)	Pb-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
1	N.W. 60 one mile west of Bartow, Polk County	1100	76	0.03						
2	N.W. 60 two miles west of Bartow, Polk County	551	680	1.86						
3 4	Ridge Wood Rod and Gun Club, 3 miles east of Mulberry, Polk County	170	2880	1.71	0.7	0.01	0.0	0.0	12	23
5	N.W. 540 five miles N.E. of Mulberry, Polk County	300	210	0.48						
6	N.W. 5404 one-half mile south of Highlands City, Polk County	155	95	0.49						
7	1-1/2 miles north of Bartow, Polk County	200	970	0.43						
8	N.W. 60 two miles east of Bartow, Polk County	-	3060	2.18	1.5	0.74	0.0	0.1	5	27
9	N.W. 27 one and one-half miles south of Alturas, Polk County	-	1030	0.69						

(continued)

Table IV (continued)

Privately Owned Wells - Central Florida

Sample Number	Location	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (pc/l)	α Th (pc/l)	Pb-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
10	N.W. 17 one mile south of Airbase, Polk County	35	3550	4.5	0.9	0.38	0.6	0.1	5	13
11	N.W. CO two miles east of Mulberry, Polk County	-	3240	0.61						
12	International Minerals & Chemical Co. (Bonnie Plant), Polk County	900	860	0.40						
13	0.1 miles east of Pebble Mine Rd. on Pebbledale Rd., Polk County	CO	3890	0.12						
14 15	1/2 mile west of CCA on Pebbledale Rd., Polk County	-	990	2.35						
1 16	N.W. CO at Jct. S.R. 555, Polk County	-	18,200	0.21	0.1	0.06	1.2	0.4	0.9	15
17	Bartow, CO Homer St. Polk County	80	1010	1.19						

(continued)

Table IV (continued)

Privately Owned Wells - Central Florida

Sample Number	Location	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (μg/l)	α Th (pc/l)	Po-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
18	International Minerals Chemical Co., Hardee Plant, Polk County	92	8370	2.70	2.2	0.03	0.8	0.2	10	14
19	Homeland Rd. 1-1/2 miles north of Homeland, Polk County	98	4730	4.21						
20	One mile south of Lutrey on Homeland Rd., Polk County	200	4160	1.07						
21	H.W. 17. 1-1/2 miles south of Bartow, Polk County	89	4190	1.04						
22	H.W.17. 3 miles south of Bartow, Polk County	160	5000	1.99	1.2	0.00	0.5	0.2	6	10
23	H.W. 555. One mile south of intersection of H.W. 555 and H.W. 640, Polk County	70	46,000	1.89	0.4	0.03	3.4	1.4	2	16
24	Gulf Co. Test Deep Well, Apopka, Florida, Polk County	800	1750	1.14						

(continued)

Table II (continued)

Privately Owned Wells - Central Florida

Sample Number	Location	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (µg/l)	α Th (pc/l)	Pb-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
25	Swift Co. well D-3, one mile west of Swift Co., Polk County	1100	2000	1.78	1.4	0.04	0.3	0.0	5	16
26	Minute Maid Co., two miles west of Agricola	-	28,800	49	11	0.37	7.6	1.5	75	194
27 28	Off Davis Rd. two miles west of Ft. Meade, Polk County	105	5780	5.22						
29	Davis Rd., 2-1/2 miles west of Ft. Meade, Polk County	-	22,700	76	4.2	0.58	3.7	0.8	97	144
30	H.W. 17, 1/2 mile north of Ft. Meade, Polk County	97	9750	0.21						
31	H.W. 17, 1/2 mile north of Ft. Meade, Polk County	187	10,850	5.13						
32	Homeland, Polk County	105	4480	2.68						
33	Homeland, Polk County	-	4130	2.41						
34	Homeland, Polk County	88	2310	2.15						

(continued)

Table IV (continued)

Privately Owned Wells - Central Florida

Sample Number	Location	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (μg/l)	α Th (pc/l)	Po-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
35	Durant Section - Durant Rd. at Turkey Creek, Hillsborough County	201	1860	1.41						
36	Intersection of H.W. 640 and Kenyon Rd., Hillsborough County	90	2490	1.11						
37	H.W. 60, 6 miles west of Mulberry, Hillsborough County	150	3040	-						
38	S.R. 60 and Coronet Rd., 4-1/2 miles west of Mulberry, Polk County	200	6270	3.84	2.4	0.03	0.6	0.1	10	-
39	H.W. 60, 3 miles west of Mulberry, Polk County	96	3350	0.16	-	-	0.3	0.1	1.0	0.0
40	2 miles east of Mulberry, Polk County	96	4260	0.02	-	-	0.2	0.1	0	0
41*	Kelly Rd. and H.W. 27A, 1 mile south of Frost Proof, Polk County	105	32	3.9						

(continued)

Table IV (continued)

Privately Owned Wells - Central Florida

Sample Number	Location	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (μg/l)	α Th (pc/l)	Pb-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
42*	H.W. 27A, 2 miles south of Frost Proof, Polk County	37	85	1.2						
43*	H.W. 27A, 3 miles north of Sebring, Highlands County	300	3830	2.3	-	-	0.2	0.2	5	13
44*	H.W. 27, 7 miles south of Sebring, Highlands County	69	23	1.42						
45*	Grassy Lake, one mile north of intersection of H.W. 27 and H.W. 70, Highlands County	46	76	5.4						
46*	H.W. 70, 2.5 miles west of Desoto-Highlands County line	-	1250	0.67						
47*	Intersection of H.W. 70 and H.W. 760 east of Arcadia, Desoto County	268	3500	8.4	0.9	0.08	0.4	0.1	20	49
48*	Brownville, Desoto County	-	1100	1.22						

(continued)

Table IV (continued)

Privately Owned Wells - Central Florida

Sample Number	Location	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (µg/l)	α Th (pc/l)	Pb-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
49	H.W. 17, one mile north of Wauchula, Hardee County	85	4040	0.44	0.8	0.09	0.1	0.1	2	13
50*	H.W. 39, at Crystal Springs, Pasco County	36	470	0.82						
51*	H.W. 50, 2 miles east of Winter Garden, Orange County	-	365	0.49						
52*	H.W. 4390, 1.4 miles south of H.W. 50, Orange County	-	2780	2.33	0.1	0.04	0.0	0.1	5	5
53*	H.W. 17, 2 miles south of Kissimmee, Osceola County	60 - 70	153	-						
54*	H.W. 17, 5 miles south of Kissimmee, Osceola County	90 - 115	870	2.17						
55*	H.W. 17, south of Kissimmee, Osceola County	74	1350	0.43						
56	1.5 miles west of Haines City off H.W. 92, Polk Co.	200	2340	3.9						

(continued)

Table IV (continued)

Privately Owned Wells - Central Florida

Sample Number	Location	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (μg/l)	α Th (pc/l)	Pb-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
57	3.5 miles east of Lakeland off H.W. 92, Polk County	162	1860	2.7						
58	3.5 miles east of Lakeland off H.W. 92, Polk County	53	2610	0.75						
59	3.5 miles east of Lakeland off H.W. 92, Polk County	150	6210	-						
60	H.W. 542, one mile east of Lakeland, Polk County	27	10,000	1.20	1.4	0.04	0.7	0.4	1.9	0
61	Intersection of Fields Rd. and H.W. 542 east of Lakeland, Polk County	287	3810	1.89						
62	Old Auburndale Rd. 4 miles east of Lakeland, Polk County	120	2410	3.58						
63*	H.W. 92, 1.75 miles west of Plant City, Hillsborough County	134	550	0.03						
64*	H.W. 92, 9 miles east of H.W. 579, Hillsborough County	150	240	0.02						

(continued)

Table IV (continued)

Privately Owned Wells - Central Florida

Sample Number	Location	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (ug/l)	α Th (pc/l)	Po-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
65*	Intersection of H.W. 301 and Palm River Rd., Hillsborough County	80	2020	0.46						
66*	River View, Hillsborough County	-	750	0.30						
67*	H.W. 301, .75 mile south of Alafia River Bridge, Hillsborough County	-	784	2.93						
68*	H.W. 301, 2.5 miles south of Riverview, Hillsborough County	96	630	1.73						
69	H.W. 672, 8 miles west of Pienic, Hillsborough County	187	3400	0.32	1.4	0.04	0.2	0.1	0.4	4
70	Intersection of H.W. 672 and H.W. 39 at Pienic, Hillsborough County	-	7650	0.28	0.8	0.01	0.6	0.1	6	0
71	Intersection of H.W. 674 and H.W. 39 at Ft. Lonesome, Hillsborough Co.	-	2650	0.33					0.3	0

(continued)

Table IV (continued)

Privately Owned Wells - Central Florida

Sample Number	Location	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (μg/l)	α Th (pc/l)	Pb-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
72	U.S. 630, 1.7 miles west of Armour Jct. Mulberry, Polk County	143	11,300	7.41	1.6	0.04	1.3	0.3	12	-
73	4 miles south of Mulberry on U.S. 37, Polk County	200	5120	2.14	1.4	0.11	0.3	0.2	-	-
74	Bradley Jct., 6.5 miles south of Mulberry, Polk County	183	7330	3.90						
75	Bradley Jct., 7 miles south of Mulberry, Polk County	-	2070	0.11	1.4	0.03	0.4	0.1		
76	One mile south of Bradley Jct., Polk County	80 - 90	9460	4.32						
77	Intersection of new and old U.S. 37, Polk County	-	3300	1.31						
78	Old U.S. 37 south into Bradley Jct., Polk Co.	15	7600	19						

(continued)

Table IV (continued)

Privately Owned Wells - Central Florida

Sample Number	Location	Depth of Well (ft)	Rn-222 (pc/l)	Ra-226 (pc/l)	U (µg/l)	α Th (pc/l)	Po-210 (pc/l)	Po-210 (pc/l)	Gross Alpha (pc/l)	Gross Beta (pc/l)
79	Bradley Jct., Polk Co.	-	1480	1.31						
80	Rolling Hills, Polk County	-	6550	2.3	1.4	0.04	0.7	0.3		
81	Oak Terrace, Polk Co.	-	8680	4.6						
82	Oak Terrace, Polk Co.	-	8430	0.0						

* Considered outside of area.

Table V

Miscellaneous Samples

Sample Description	Rn-222 (pc/l)	Ra-226 (pc/l)
Lithia Springs - Thermal Springs	2360	0.65
Alafia River - State Route 640 at Bridge (State Sampling Point A4)	45	0.21
American Cyanimid Slimes Pond Water	12	0.17
Natural Well - Highway 640 at Bridge over South Fork Alafia River	300	2.05
International Minerals Corporation Cypsum Pond Water (at Spillway)	240	112.90
Peace River at Saddle Creek	20	0.65

Table VI

Inorganic Chemical Analyses, ppm - Municipal Supplies

Sample Number	pH	Alkalinity as $CaCO_3$	Nitrate Nitrogen	Total Hardness	Conductivity *	Total Phosphate	Sulfate	Total Solids	Fluorides
85	7.7	110	0	120	120	0.03	10	134	0
88	7.6	78	0	88	75	0.15	2.0	98	0
93	7.6	168	0	174	165	0.29	3.0	114	0.4
94	7.5	108	1.6	109	120	0.26	5.0	324	0
97	7.4	73	1.2	86	96	0.41	3.0	144	0
99	7.9	104	-	112	110	0.23	4.5	164	0.3

* μ mhos at 25°C

Table VI

Inorganic Chemical Analyses, ppm - Privately Owned Wells

Sample Number	pH	Alkalinity as $CaCO_3$	Nitrate Nitrogen	Total Hardness	Conductivity*	Total Phosphate	Sulfate	Total Solids	Fluorides
4	7.7	82	0	91	83	0.07	4.5	128	0.5
8	7.4	246	0	260	230	0.17	10	324	0.7
10	4.1	0	7.4	60	110	0.03	4.5	150	0.1
16	6.3	18	0	26	46	2.8	15	90	0.5
18	7.3	78	0	83	83	0.12	2	112	0.4
22	7.5	136	2.6	164	175	0.44	72	242	0.3
23	6.3	20	0	23	41	2.6	15	120	0.3
25	7.3	224	0	224	220	0.03	4.5	334	1.0
26	4.7	4	26.0	360	520	0.23	220	952	1.2
29	5.1	4	16.0	179	215	0	120	363	1.2
33	7.9	166	0	179	160	0.13	1.5	220	0.3
39	6.9	44	4.0	57	60	0.50	5.5	124	0
40	7.4	184	0	8	200	0.13	3	294	0.3
43	7.1	78	0	60	60	0.40	2.0	108	0

(continued)

Table VII (continued)

Inorganic Chemical Analyses, ppm - Privately Owned Wells

Sample Number	pH	Alkalinity as $CaCO_3$	Nitrate Nitrogen	Total Hardness	Conductivity *	Total Phosphate	Sulfate	Total Solids	Fluorides
47	7.8	172	0	200	215	0.13	4.5	124	1.7
49	7.6	124	0	75	102	0.61	1.5	134	0.4
52	7.5	120	0	112	120	0.41	2.0	98	0.2
60	7.8	188	-	200	200	0.16	4.5	270	0.2
63	7.7	143	0	143	135	0.09	7.5	168	0.3
70	7.9	98	0	117	90	0.15	4.0	106	0.6
71	6.7	42	0	29	48	4.10	5.0	96	0.6
72	7.8	178	0	169	155	0.27	3.0	238	0.4

* μ mhos at 25°C

is masked by the extreme ranges of the concentrations, particularly the radon concentration. However, if the radon and radium concentrations are ranked in a decreasing order, and a Spearman's rank-order correlation P (Rho) calculated, an observed value of 0.347 for 100 pairs of data (private and municipal water supplies) is obtained. At the $\alpha = 0.001$ critical level for $N = 100$, the upper limit due to chance is 0.321. Thus, it can be seen from this test that there is a definite, although slight, correlation between the radon and radium levels.

Secondly, are the observed radon and radium levels in untreated water supplies outside the active mining area different from the observed levels within the area? Again a casual glance does not confirm or deny this.

If, however, we again rank the sample values collectively in a decreasing order (N_1 to N_T) and apply the Wilcoxon equation to test whether or not the two groups are from the same population or two distinct populations, a Z-statistic can be calculated from the equation:

$$Z = \frac{\Sigma R_1 - \frac{n_1(N_T + 1)}{2}}{\sqrt{\frac{n_1 n_2 (N_T + 1)}{12}}}.$$

where n_1 = Number of samples outside the area

n_2 = Number of samples inside the area

N_T = $n_1 + n_2$

ΣR_1 = Summation of the rank position of the samples outside the area,

we observe a $Z_{Ra^{226}} = 1.3$; $Z_{Ra^{222}} = 3.7$.

Comparing these calculated values to a Z-statistic table, it can be shown that the Ra^{226} concentrations in the water samples between the two areas are not significantly different at the 95% confidence level ($\alpha = 0.05$). This, however, does not imply that the Ra^{226} concentrations in the earth are statistically equivalent. On the contrary, since the Ra^{222} concentrations in the water samples are significantly different at the 95% and even at the 99.9% confidence level and since radon, an inert gas, is readily soluble in water whereas its precursor, Ra^{226}, is probably so chemically bound as to be relatively insoluble, it can be concluded that higher Ra^{226} deposits coincide with enriched phosphate deposits.

The Federal Radiation Council (FRC) has defined ranges for total daily Ra^{226} intake and recommended countermeasures. These are:

Range I -	0-2 pc	Periodic confirmatory surveillance
Range II -	2-20 pc	Quantitative surveillance and routine control
Range III -	20-200 pc	Evaluation and application of additional control measures.

Assuming a 2-liter daily intake of water, a water supply whose Ra^{226} concentration is 10 pc/l would place an individual at the upper limit of Range II, disallowing any other ingestion of Ra^{226} from other sources (food, air). The Public Health Service Drinking Water Standard has been set at a value of 3 pc/l.

Reviewing the data, two municipal water supplies are above the 3 pc/l level but below 10 pc/l. In the case of the privately owned wells, 12 wells are greater than 3 pc/l and less than 10 pc/l; three wells are greater than 10 pc/l (19, 49, and 76 pc/l).

It should be pointed out that at present there is no accepted standard for Rn^{222} in water. A number of workers have addressed themselves to the question and have suggested possible maximum permissible concentrations for Rn^{222} in water.

The Maine State Department of Health and Welfare, after reviewing several articles on this subject, established tentative guidelines for permissible concentration of radon in water to be used until a firm standard is set. These guidelines are 100,000 pc/l occupational dose, 18,000 pc/l for an individual in the population, and 16,000 pc/l for public water supplies. The above figures are about 10% lower than those suggested by Hursh and co-workers.*

Only four privately owned wells are above this 18,000 pc/l Rn^{222} whereas no municipal wells even approach this figure. Aeration would substantially reduce the radon concentration by approximately 50-75% to within these guidelines as deduced from the data given in Table III, Sample Numbers 83, 90, and 98.

Radon values should be evaluated in terms of sample collection techniques. Radon values for pumped wells probably have little interpretive

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* Hursh, John B., et al. Health Physics, Vol. 11, p. 463-76 (1965).

significance; however, such values may be useful for rapid reconnaissance of many wells over a large area to identify those wells that should be sampled for radium analysis.

In regard to the chemical constituents of the water, none of the determined elements exceeds the limits set forth in the Public Health Service Drinking Water Standards.

Recommendations

As a result of the study, the following recommendations are submitted:

1. That the recommendations set forth by the FRC be implemented; that is, all well waters used for domestic consumption whose Ra^{226} concentrations range from 1 - 10 pc/l be routinely monitored. All wells above 10 pc/l should be routinely monitored and corrective action taken to decrease the level to within Range II, and hopefully to within Range I of the FRC.

2. Wells previously showing high radium concentrations should be resampled and efforts made to identify the aquifer supplying water to them.

3. In some areas of Florida, ground-waters contain excessive radium with respect to parent uranium. An effort should be made to determine if a natural disequilibrium exists in the "principal artesian aquifer" and if so, the degree. Determination of the natural background disequilibrium will permit identification of water to which excess radium has been added from outside sources.

4. The characteristics of the effluents from the fertilizer industry should be determined and a radium and uranium balance should be done for plant operations. Surface-water courses near the plants and ground-water for all municipal wells down the hydraulic gradient from the plant should be sampled and analyzed also for radium and uranium.

Summary

Ra^{226} and Rn^{222} concentrations in water supplies, both municipal and private, were determined in and around the active phosphate mining area. A correlation between radon and radium concentration does exist but is yet empirically undefined. The radon concentrations in well water outside the phosphate mining area are lower than those within the area. Recommendations for further study have been incorporated.